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Permeability and additive absorption and extraction in lubricating greases

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Department:

PERMEABILITY AND ADDITIVE ABSORPTION AND EXTRACTION IN LUBRICATING GREASES

BY

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SUMMARY AND CONCLUSIONS

A permeability apparatus was used to measure the permeability coefficients of eight Lithium-Calcium greases and ten Baragel greases in which the viscosity and type of the oil component were varied. The oil present in each grease was used for its permeability measurement.

An improved sample packing technique was developed to improve the repeatability of permeability measurements. Repeatability of ±3% was achieved. In general the permeability coefficients of the non-soap Baragel greases were higher than those of the lithium-calcium greases with comparable oil components, and those of greases containing paraffinic oils were higher than these containing naphthenic oils. The effect of the viscosity of the oil from which the greases were made on permeability was less certain. With naphthenic oils, permeability increased with increase in viscosity in both the lithium-calcium and the Baragel greases. With paraffinic oils, the permeability coefficient was much less sensitive to oil viscosity for both thickeners.

Another set of experiments aimed at the measurement of the absorption and extraction of small percentages of a grease additive were performed using the same apparatus. One lithium and one Baragel grease were used. Phenyl-α-naphthylamine, the additive

used, can be analyzed in the infrared spectrophotometer to concentration levels as low as 0.05%. Experiments in which grease containing additive was extracted by oil without additive were performed and vice versa. Additive mass balances were determined from the infrared analyses.

The amount of additive absorbed at equilibrium by the Baragel grease was greater than for the lithium grease, but the initial rates of absorption were about the same. The Baragel grease absorbed a calculated 1.79% of additive as compared to 0.90% for the lithium grease.

In the additive extraction experiments, grease initially containing 1.38% additive held 0.23% (Baragel) and 0.18% (lithium) in equilibrium with pure oil. The initial rate of extraction was greater for the lithium grease.

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I. INTRODUCTION

A lubricating grease can be defined as: "A solid or semi-fluid lubricant consisting of a thickening agent in a liquid lubricant. Other ingredients imparting special properties may be included."(1) The most commonly used lubricating greases are made from petroleum oils with soap or clay based thickeners.

Greases or their equivalents have been made for several thousand years. Egyptians used lime soap materials for the lubrication of chariot wheel axles as early as 1,400 B. C. (2). These products were crude partially saponified fatty materials, and similar products were used for many centuries thereafter until crude petroleum oil was found about a hundred years ago.

The Industrial Revolution in the West and its emphasis on machinery raised, for the first time, the problem of lubrication of many kinds of machines. However, it was not until the advent of the automobile that any great demand for special greases arose. In more recent years, the use of higher precision, higher speed, heavier loaded and more specialized machinery necessitated the development of specialized greases to supplement or replace calcium soap greases. Extensive

research and product development on grease began just before the World War II and has substantially increased ever since as quality demands became more and more stringent. Sodium, lithium, barium and calcium complex soap thickeners, clay based thickeners, and high temperature-stable pigment thickeners, have been used in recent years along with synthetic oils such as the diester, silicone, and polyphenyl ether types (3). The widespread use of low concentrations of additives for oxidation inhibition, rust protection, and load carrying enhancement, etc., has also had a major effect in improving grease quality.

Although many highly useful formulations have been developed and characteristics unthought of 25 years ago are now readily available in commercial products, there is still a great deal of uncertainty about the fundamental nature of the thickener systems from which greases are formed. Here as in many areas, technology has outstripped fundamental knowledge. Much information has been gained on how to produce certain desired effects in formulations, while an understanding of the causes of these effects has been difficult to obtain.

Published information on the effect of oil viscosity and type on thickener structure and grease properties is scarce. Grease formulators' experience and rules of thumb have led to the many

good commercial products available, but only a few systematic studies have been reported (4, 5, 6, 7, & 8). The relative importance of viscosity of the oil in which the thickener is formed and its solvency properties for the thickener are only barely understood qualitatively. It is generally agreed that moderate viscosity oils of a naphthenic type give the most satisfactory grease properties for most thickener types. An oil which is too naphthenic, however, is considered undesirable.

One of the problems that grease makers face is separation of oil from grease in storage, in pumping, and in service. The tendencies for this to occur vary with the nature of both the thickener and the oil. The degree of separation also depends on the nature of the service. The desired level of separation is in considerable dispute. Baker (9) claims that a good grease should possess the property of low initial rate of oil separation but should have the property of being able to give up a high proportion of its oil for long ball bearing life. Several authors (4, 6, 9, 10, & 11) have shown that the nature of the grease structure will affect oil separation.

The permeability of a grease refers to its ability to allow lubricating oils to permeate through the grease structure. Thus

permeability measurements can give some insight into the nature of the grease structure and the "tightness" with which the thickener holds the oil(12). An apparatus for measuring permeability in greases was developed recently(12). In structural studies, it may complement quantitatively the qualitative results available from the electron microscope.

With this in mind, this research was aimed at studying the effect of the nature and the viscosity of mineral oil in which the thickener structure is formed on the permeabilities of a series of greases made with different oils but the same thickener(lithium soap). In addition, the effect of the thickener on the permeabilities of greases made with these same oils was studied using a clay-base thickener in greases having the same mineral oils as the lithium soap greases. Until recently(13), no permeability data on greases made with this type of thickener had been reported. An important part of the experimental effort was to improve the repeatability of permeability measurements by changes in the experimental procedure.

The mechanism of additive action in lubricating greases is also not clear. The effect of additive concentration on improvement of particular properties is also not understood. Furthermore, some additives affect the mechanical stability of a grease

and presumably its structure at concentrations as low as 0.1% while others have little effect at much higher concentrations. As a first step in studying additive effects, it is desirable to determine whether the additives, usually present in amounts less than 2%, are absorbed on the thickener surface, whether they are in oil solution, or whether a combination of these prevails. Accordingly, a set of extraction experiments, with oil free from additive and grease containing additive, and a set of absorptive experiments, with grease free of additive and oil containing additive, were also run.

II. LITERATURE REVIEW

A. Grease Permeability.

In 1960 Sisko and Brunstrum (12) designed and used a permeability apparatus for the measurement of the permeability of grease in order to study grease structure. It involves measurement of the change in height of a column of oil supported over a grease sample through which the oil is permeating. The apparatus is described in detail in the Description of Apparatus section and is shown in Figures (2, 3, and 4). Permeability data obtained for several greases were also presented. For a series of greases, they found that oil separation using the ASTM test method and the ratio of permeability to viscosity are in the same order, but their relations are not linear. They also found that the permeability coefficient of the grease decreased with increasing percent of worked rheopectic grease in total grease or a higher percent of more highly dispersed soap thickener.

The calculations of permeability are based on Darcy's Law (12):

$$V_s = \frac{BP}{\mu L}$$

where:

V_s = effluent rate per unit cross-sectional area, cm per sec

P = pressure drop across the sample, dynes per cm^2

L = thickness of the sample, cm

μ = viscosity of the oil, poises

B = permeability coefficient, cm^2

The permeability coefficient, B, may also be described as cm^3 per sec of oil of unit viscosity flowing through a unit volume of the grease under a pressure drop of 1 dyne per cm^2. Darcy's Law in the above form, $V_S = \frac{BP}{\mu L}$, can be transformed into a more convenient form (14) as shown below.

According to the law of continuity, the volume rate of oil flowing in the pipette column of the apparatus must be equal to that flowing through the grease sample at any cross section, assuming the density of the oil being constant,

$$A_p V_p = A_S V_S$$

where,

A_p = the cross sectional area of the pipette

A_S = the cross sectional area of the sample

V_S = the velocity of the oil in the sample

V_p = the velocity of the oil in the pipette

assuming uniform flow through the sample and rearranging this equation,

$$V_S = \frac{A_p V_p}{A_S} = \frac{A_p}{A_S} \frac{dh}{dt}$$

where h is the height of the oil level above the top of the grease. The pressure drop across the sample is ρhg.

where ρ = density of the oil, in gm per cc
g = acceleration of gravity, in cm per sec^2
h = height of the oil level, in cm

substituting these values into Darcy's Law in the above form gives,

$$\frac{A_p}{A_s}\frac{d(h)}{dt} = \frac{B\,h g \rho}{\mu L}$$

the group μ/ρ is the kinematic viscosity ν.

making this change and solving for B gives

$$B = \frac{A_p \nu L}{A_s g}\frac{d(h)}{dt}$$

or $$B = \frac{A_p \nu L}{A_s g}\frac{d\{\ln(h)\}}{dt}$$

For a particular apparatus geometry and oil viscosity of the permeating oil, the group $\frac{A_p \nu L}{A_s g}$ is constant and can be called K, and then $B = \frac{K\,d\{\ln(h)\}}{dt}$. Plots of ln(h) vs t are generally linear, and from the slope, values of B can be computed.

Ewbank and co-workers (15) have studied grease permeability in the above apparatus and have showed the validity of Darcy's Law as applied to the permeability of greases. They found that the effect of varying the thickness of grease sample on permeability coefficients is small, ranging from 0 to 30% for changes of sample thickness by a factor of 2 1/2. They also

found that the viscosity of the permeating oil through the grease had no effect on the permeability coefficient for any given type of oil. Their results for different oil types were not conclusive.

Neither Ewbank et al., nor Sisko and Brunstrum described the repeatability of their measurements. However, unpublished data of Zakin and Peterson (16) showed maximum deviations of 18% of individual values from the mean of three runs.

Recently, considerable work has been done to improve the repeatability and reproducibility of results from permeability measurements (17). Suggestions have been made to use a metal table to support screens in a flat position during filling to prevent non-uniform sample thickness and to seal the ground joint of the apparatus with Duco cement to prevent leakage through the joint, and to groove the inside face of the rataining ring to prevent oil leakage. A revised drawing of the permeability apparatus and associated equipment which incorporated these suggestions has been prepared (17). However, only this same laboratory has used this new apparatus and procedures, and the degree of improvement remains to be checked.

B. ADDITIVES IN GREASES

Boner(1) has classified grease additives, according to their functions, into ten categories, such as oxidation inhibitors, corrosion and rust inhibitors, etc. The mechanisms by which additives in grease function are only vaguely understood. The level of additive required in grease is usually determined empirically.

Most additives contain active functional groups. These groups can be used to identify, qualitatively and quantitatively, the specific chemical groups in a compound from their infrared spectra. Characteristic absorption bands of a chemical group appear in the infrared spectra at particular wavelengths. The amplitude of the absorption bands are proportional to the amount of that group present in the compound and can be utilized as a quantitative method of analysis for the compound.

However, little has been published on the application of infrared spectrophotometry for analysis of additives in greases. Wiberley, Bauer, and Cox(18) have made a systematic study of the identifications of several metal soap greases by infrared analysis. Despite the paucity of published information, infrared is widely used in industry for qualitative and quantitative analysis of additives in greases(19).

III. EXPERIMENTAL

A. PREPARATION OF GREASE SAMPLES.

1. Lithium-Calcium Stearate Greases.

Eight samples of lithium-calcium stearate greases were obtained from the Socony Mobil Oil Company Research Laboratories. These were the same greases listed in Reference(10). They were prepared by a pilot plant low temperature(300°F) spray technique described in that reference.

The greases contained 7% by weight of a lithium-calcium soap of hydrogenated soya bean fatty acid and 0.2% of an oxidation inhibitor. The soya bean fatty acid contains about 85% stearic acid; the remainder is mainly palmitic acid.

A series of naphthenic blends was used to give greases having oil viscosities ranging from 117 to 2450 centistokes at 70°F (blends A, B, and D). These oils were similar in composition but varied in molecular weights. Another set was prepared with a series of solvent refined high VI paraffinic blends of about the same viscosity(blends E, F, and G). A solvent refined naphthenic (J) and a Pennsylvania(K) were also used. Compositions and properties of the oil blends are listed in Tables I A and I B.

Viscosity index(VI) is an arbitrary standard to express the

TABLE IA

Characteristics of Blending Oils

Blending Oil	Type	Viscosity, Cstokes(100°F)	Approx. VI
1	100 second Naphthenic pale oil	22.9	2
2	Naphthenic bright stock	1089	< 0
3	200 second solvent refined paraffinic neutral	44	98
4	Solvent refined paraffinic bright stock	538	97
5	500 second solvent refined naphthenic	105	70
6	Conventional Pennsylvania neutral	32.4	104
7	Conventional Pennsylvania bright stock	528	101

TABLE IB

Oil Blends in Greases Tested

Naphthenic Blends

Oil blend	% 100 second naphthenic pale oil	% naphthenic bright stock	viscosity, Cstoke @70° F	VI
A	78	22	117	36
B	51	49	345	30
C	33	67	880	13
D	15	85	2450	-4

Solvent Refined Paraffinic Blends

Oil blend	% 200 second solv. ref'd paraff. neutral	% solv. ref'd paraff. bright stock	visc, Cstoke @ 70° F	VI
E	100	00	108	98
F	60	40	330	94
G	33	67	680	97
H	00	100	1850	97

J	100% 500 second solvent refined naphthenic	320	70
K	50% Pennsylvania neutral, 50% Pennsylvania bright stock	320	105

relative change of viscosity with temperature. The standard of comparison is based on Pennsylvania oils refined by the sulfuric acid method. These oils were rated 100 for this property; Gulf Coast naphthenic oils were rated 0. The higher the viscosity index of the oil the less the oil thins out as the temperature rises. High VI oils also thicken less rapidly as the temperature drops. In general oils high in paraffinic components have high VI's. They are obtained by refining highly paraffinic base stocks(Pennsylvania oils) or by selective extraction of more naphthenic stocks to raise the paraffinic level in the finished oil(solvent refined naphthenic oils).

Viscosity index is, therefore, widely used as a rough measure of the composition(paraffinicity) of an oil or an oil blend, particularly at the high end of the scale. Oils A, B, C, and D are all low VI oils and naphthenic by these standards. Oils E, F, G, H, and K are all highly paraffinic, and oil J is moderately paraffinic.

2. Lithium hydroxy stearate greases of the following formulation were prepared:

Materials	Weight, gm
Hydrogenated castor oil fatty acid	118.0
Lithium hydroxide monohydrate	20.0
Hydrogenated soya bean fatty acid	48.0
Mineral oil(500 Saybolt sec solv ref Coastal-60VI, see oil J, Table I B)	1240.0

Hydrogenated castor oil contains 80% lithium hydroxy stearate and about 20% of stearic acid. This formulation contains about 8% fatty matter, slightly less than 40% of this is stearic acid and slightly less than 60% hydroxy stearic acid.

All of the fatty material was mixed with 620 gm of the oil in a 5-pound grease kettle (Figure 1), and agitation and heating were started. The lithium hydroxide was dissolved in 100 cc of hot water and was added to the kettle after the fatty acids had melted at about 77°C. This soap-oil mixture was then heated slowly to 120°C to drive off the added water and the water of reaction, and then it was heated rapidly to the melt which occurred at about 190°C. The remaining portion of charge oil was then added to the melt; if any congealing occurred, the grease was reheated to the melt. The heat was removed, and the grease allowed to cool without agitation. For the sample containing additive (LGA), 20 gm of phenyl-α-naphthyl amine (PAN), a common oxidation inhibitor additive was dissolved in 100 gm of lubricating oil by heating the mixture to about 80°C. It was added to the bulk of grease when the grease cooled down to 100°C. The mixture was agitated for another 30 minutes at this stage to ensure uniform dispersion of the additive in the grease. All products were then homogenized by passing through a Morehouse

Figure 1. Grease-Making Kettle with Heating and Stirring Units

Mill twice.

The thickener concentration used was chosen to give products of about 300 penetrations for all oil blends. No penetrometer was available with which to measure consistency. The greases appeared to be in the No. 1 to No. 2 NLGI consistency range as judged by finger penetrations.

3. Baragel Greases.

Baragel is the reaction product of sodium montmorillonite and a difatty quaternary amine and a small proportion of benzyl fatty quaternary amine. The ultimate particle size is 0.5 to 1.0 microns in diameter by 0.002 to 0.004 microns thick.

Ten non-soap Baragel greases were prepared. Compositions and properties of the oil blends are listed in Table IB. They are the same as those used in reference (10).

The formula for the Baragel greases is shown as below:

	charge weight, gm	final percent
Baragel	50.0	5.0
pentaerythritol	5.0	0.5
water	20.0	-
acetone	15.0	-
oil blend	945.0	94.5

The Baragel and acetone were added to the oil blend in the grease kettle and mixed. This mixture was then agitated in a

Cowles Mixer at 2,000 rpm for two minutes. The resulting thickened mixture was heated with mixing in the grease kettle to 83°C. At this time 5 grams of pentaerythritol dissolved in 20 grams of water at 83°C was added, and the temperature raised to 110°C to drive off the water and acetone. After cooling, this mixture was again mixed in the Cowles mixer for two minutes and then passed through the Morehouse Mill three times.

For the sample containing additive, BGA, 14 gm of PAN were melted at 80°C and dissolved in the bulk of grease when it cooled down to 100°C. This mixture was agitated for another 30 minutes to ensure uniform dispersion of additive in the grease.

B-1. Description of Permeability Equipment.

The apparatus used for the permeability measurements was the same as that described by Sisko and Brunstrum (12) and is shown in Figures (2, 3, and 4).

The apparatus consists of a 5 cc pipette with a wide opening at one end and a ground glass joint at the other end. The ground joint end of pipette is connected by a bell-shaped glass adaptor to the main sample assembly. The sample is retained inside a stainless steel ring about 0.5 cm high between two millipore filters (type HA).* The filters are placed beneath and on two 40 mesh stainless steel screens which are soldered to the two retainers. The entire sample assembly is held within a pair of screw clamps. A neoprene rubber ring is placed between the bell-shaped adaptor and the sample assembly, and another ring is placed on the extended base of the adaptor to ensure a tight fit for the entire assembly.

The apparatus rests in a 400 cc beaker which, in turn, rests on a plastic rack immersed in a constant temperature water bath automatically controlled at 70°F for these experiments by a thermoregulator-relay-heater system. The water bath is heated by a 750 watt electric heating coil which is always on and whose

* Millipore Filter Corp., Bedford, Mass.

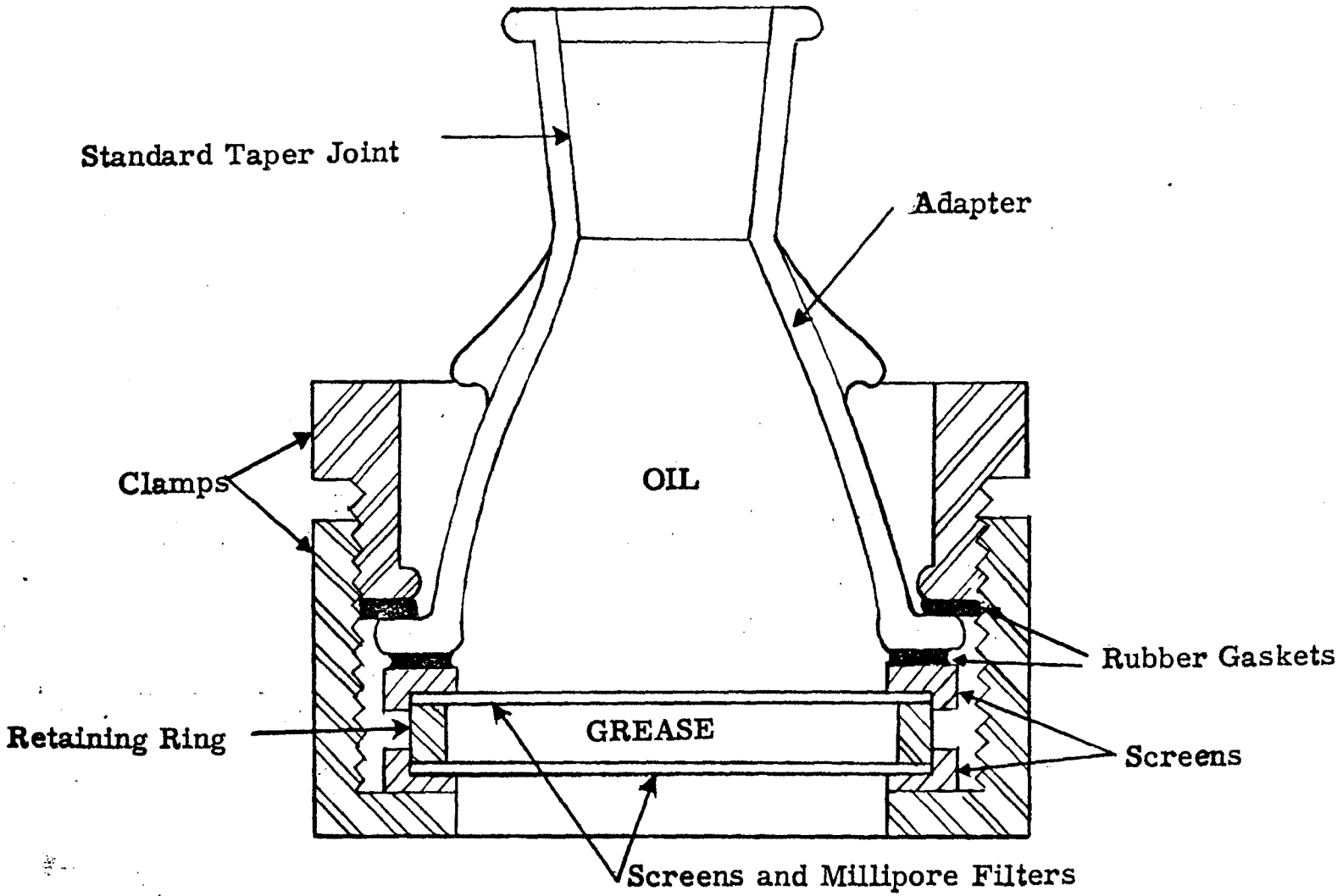

Figure 1. Permeability Apparatus Diagram

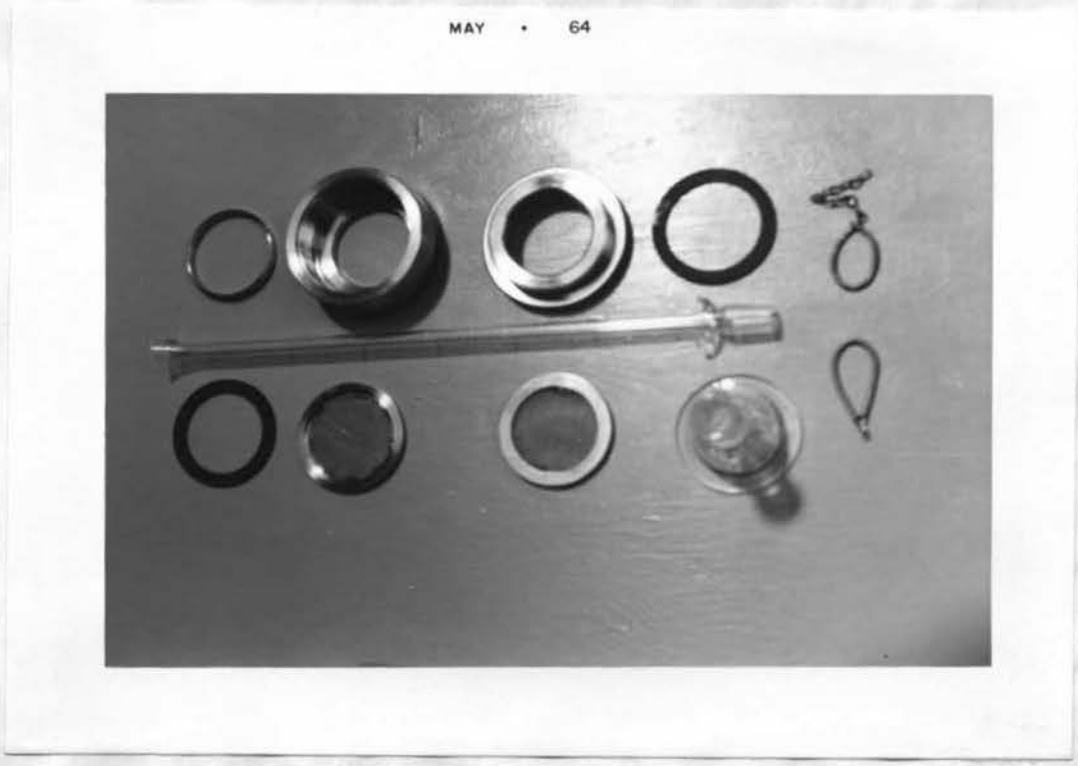

Figure 3. Disassembled Permeability Apparatus

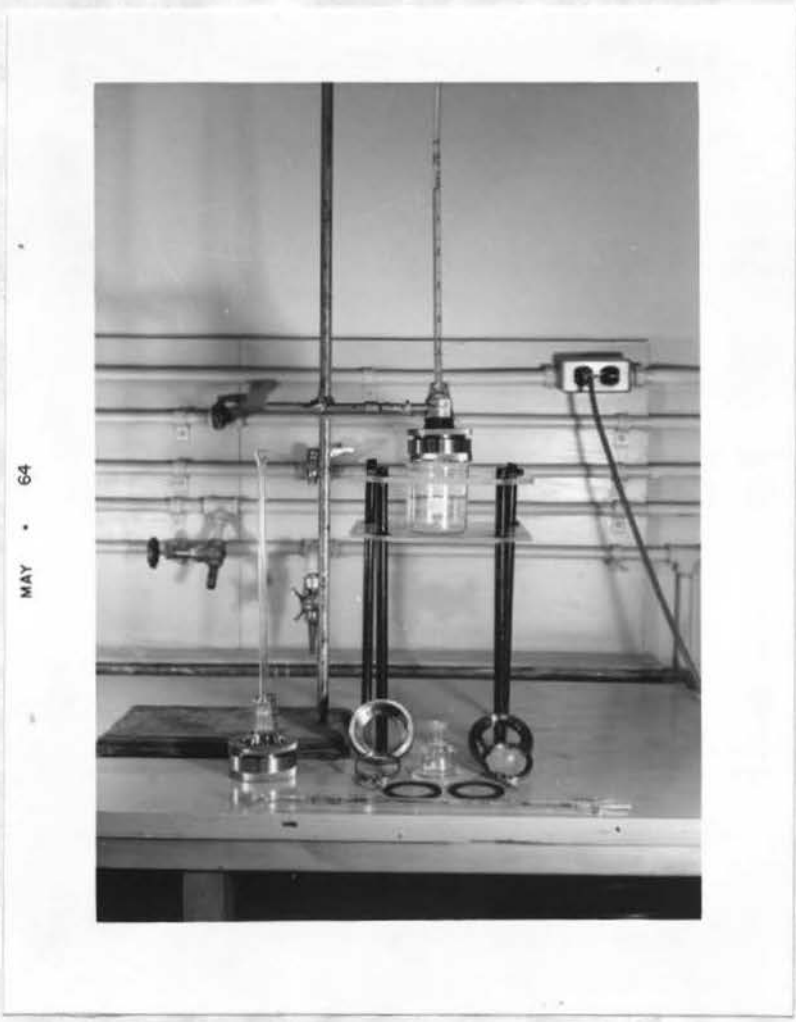

Figure 4. Permeability Apparatus: Assembled, Disassembled and Mounted on Rack

output is controlled by a variac. Another smaller heater (200 watt) is controlled by a variac and the relay. A stream of cold water continuously circulates in a copper coil and serves as a cooler. A Sargent stirrer (capacity 3 1/2 gal/min at zero head, 1550 rpm, max 1/30 hp) is provided to stir up the bath water to maintain uniform temperature distribution. Heating coil, cooling coil, and the motor stirrer are mounted on an iron rack around the water bath.

For the studies of additive extraction and absorption, the constant temperature bath was not used. Room temperature ranged from 75°F to 85°F. The apparatus rested on the top of a 250 cc beaker. Exit oil samples were collected from the beaker and the liquid clinging to the bottom of the cell.

B-2. PROCEDURES FOR PERMEABILITY MEASUREMENTS

A millipore filter paper, wetted with the same oil from which the grease was made, was placed on the bottom of the supporting screen. The retaining ring was then placed on this filter paper, and grease was packed into it either by the improved method described in the next section or with the help of a steel spatula. After all, or most, of the air bubbles were removed, a long steel spatula with a smooth edge was used to wipe off the excess grease to make the sample surface flat and smooth. Another piece of wet filter paper was carefully added on the top. Care was taken to avoid air entrapment, the top screen was then put in place. The bottom of the clamp supports the retaining ring, screen, and the sample. Above this are, in succession, a neoprene rubber gasket, the glass adaptor, another rubber gasket, and the top of the clamp (Figure 2). The clamps were then screwed together tightly by hand to a marked position. The adaptor was filled with oil, and then the pipette was mounted on the ground glass joint of the adaptor. Two springs were attached to hold the pipette tightly in place to prevent oil leakage.

The pipette was filled with oil to the 5 ml. mark. The sample was then placed in the holding rack in the constant temper-

ature bath and held at 70 °F ± 1.0 °F. The sample was held for 1 to 2 hours before starting the run to make sure any air bubbles trapped in the oil rose to the surface. A small amount of additional oil was added after all the air bubbles were removed, and the initial height reading was taken. Readings were generally made every two hours for the first 8 hours and as frequently as possible thereafter. Runs were terminated after 30 hours or when the liquid level fell below the pipette scale.

Permeability calculations for the greases were made directly from the measured data. A typical run is shown in Figure 5. No corrections for the resistance for the cell and the filter papers to the oil permeation were made as the maximum correction was less than 1% as shown by the sample calculations in Appendix A1.

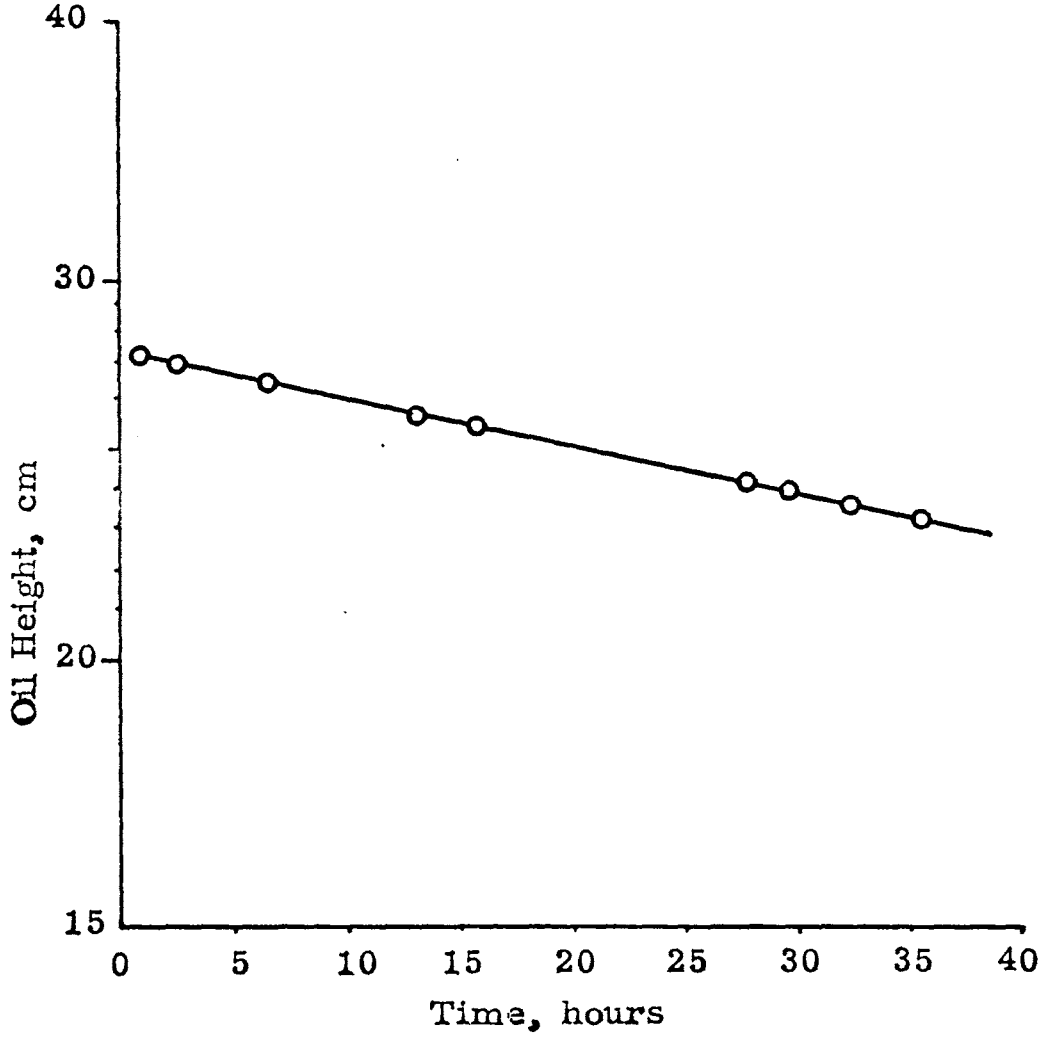

Figure 5. Oil Height vs Time Data for Baragel Grease BG

B-3. IMPROVEMENT OF PERMEABILITY TEST PACKING TECHNIQUE

One of the most serious problems in packing the grease sample is the presence of air bubbles in the sample. An attempt was made, at the beginning of this investigation, to seek a better way of packing the sample so that little or no air would be introduced into the sample. A commercial lithium base grease of suitable rigidity (about 300 penetration) was used. The general procedure was to suck the sample into an intermediate glass tube holder first, then carefully push the grease from the tube down into the sample retaining ring. The light vacuum removed some of the air in the grease and concentrated it into larger air pockets in the holder. Discharge of the grease could be controlled so as to avoid introducing these air pockets into the test sample.

A piece of glass tube, about 15 inches long and with an inside diameter of 1/4 inches, was employed as an intermediate holder. An oil-type vacuum pump was used, at first, to suck grease up from the container, but it was found that this suction force was too great. An ordinary water aspirator was found to be satisfactory for this purpose. The grease was extruded from the glass tube by compressed air or by a solid rod piston.

Rubber tubing was attached to one end of the glass tube, the other end being free to contact the bulk grease in the container. The free end of the glass tube was immersed into the bulk grease in the container as far from the grease boundary as possible. The other end with rubber tubing was then connected to a water aspirator. The rise of the grease in the glass tube was controlled by the rate of water flow. Air bubbles appear as transparent light spots in the grease in the tube. If the immersed tube loses contact with the grease and sucks air, the operation must be repeated. When the tube of grease was 2/3 full of grease, it was removed from the water aspirator first and then from the grease container.

The grease was then extruded from the tube into the sample retaining ring by means of compressed air. The air pressure was controlled by hand, by connecting the tubing to the open air outlet tightly or loosely as desired. Pockets of trapped air could be seen as they appeared. The rate could be controlled so that no new air pockets were introduced into the pile of grease on the retaining ring. Then a long steel spatula was used to sweep off the excess grease and make the sample surface smooth and flat. Several glass tube packings were needed to fill the sample volume.

This grease packing procedure gave some promising samples which appeared to be free of air bubbles. A large amount of grease in the container was essential to prevent the suction force exerted on the grease from digging out a channel long enough to reach the grease-air interface.

A factor that affects the packing is the rigidity of the grease. The procedure was developed for a grease of moderate rigidity (about 300 penetration); and it was found that greases of about this consistency were most satisfactory in the packing operation. Owing to their slow mobility, heavier greases, do not permit the air bubbles to form into pockets and to be removed. On the other hand, lighter greases picked up new air bubbles upon suction.

Repeatability of permeability coefficients using this improved technique was quite good. The maximum range of deviations from the average for three runs was ±3%.

C. ABSORPTION AND EXTRACTION OF ADDITIVE

This investigation was carried out in two ways. An extractive experiment was run in which oil without additive was permeated through grease sample containing 1.38% of additive, and an absorption experiment was run in which oil with 1.0% of additive was permeated through grease samples without additive.

1. Grease with 1.38% Additive, Oil without Additive.

The lithium hydroxy stearate grease made from the 500 second solvent refined naphthenic oil(J) and containing 1.38% PAN additive, LGA, was packed into the permeability apparatus sample retainer. Because of its heavy consistency, it had to be packed with the aid of a steel spatula. Air bubbles were driven off as much as possible during this sample packing. The same oil(J) without additive was added to the bell-shaped glass adaptor of the apparatus, the pipette was mounted on top, and the pipette was filled to the 5 cc mark. The apparatus was then put on a 250 cc beaker which rested on a rack; a laboratory ring and clamp stand were provided to hold the apparatus in place.

The extract oil which permeated through the grease sample was collected frequently for infrared spectrophotometry analysis.

The oil at the bottom of the apparatus was wiped off after each oil sample was taken. New oil was added in the pipette to maintain the oil throughput rate. The amount of oil added each time (2-3 cc) was recorded. This was taken to be the same amount of oil that permeated through the grease sample. This experiment lasted for 537 hours and 26.0 cc of oil(equivalent to about 31/2 grease volumes) were collected.

The oil samples were then analyzed in the Beckman IR5A infrared spectrophotometer for PAN concentration. The method of analysis is described in the next section.

For the Baragel grease containing PAN, BGA, the same procedures as for lithium grease were used. This experiment lasted for 469 hours and 19.7 cc of oil(equivalent to about 2 1/2 grease volumes) were collected and analyzed.

2. Grease without Additive, Oil with 1.0% Additive.

About 250 gm of mineral oil(J) with 1.0% of PAN additive was prepared for this experiment. The experimental method was essentially the same as in part 1. Oil with 1.0% additive was permeated through the lithium grease without additive, LOA, and this experiment was terminated after the exit oil contained 1.0% of additive. This experiment lasted for 339 hours and 38.5 cc

of oil (equivalent to about 5 grease volumes) were collected and analyzed.

For the Baragel grease, BOA, the test was run until about 7 grease volumes had been collected. Forty-eight samples were collected in 615 hours and analyzed for PAN concentrations.

Sample calculations from these data are shown in Appendices A-2 and A-3.

D. INFRARED ANALYSIS

In order to ascertain the additive pick up or loss of the permeated oil and the residual grease samples as described in section C, a simple, accurate analytical technique was needed to measure additive concentrations down to 0.02 % by weight. Infrared analysis was a reasonable choice provided a sensitive absorption band for the additive could be found.

1. Oil Analysis.

Several additives in oil solution were checked. Phenyl-α-naphthyl amine (PAN), paratertiary butyl catechol (Ionol), and a phosphorous containing additive (Santolube 31). PAN was selected for these experiments because concentrations as low as 0.02% by weight could be detected by examining the absorbance at a wave number of 770 cm^{-1}. At 0.05%, the peak height was about 0.3 divisions on the graph paper (on Table II). Each division is 0.05 inches. The low concentration peak at 1570 cm^{-1} was more erratic in peak height fluctuations from day to day than that at 770 cm^{-1}. Other peaks at this concentration were less sensitive.

Measurements were made with a Beckman IR5A infrared

TABLE II

Relative Height of Absorption Peak in Infrared Spectra
(Each unit = 0.05 inches)

% PAN in Oil	Wave Number, cm^{-1}			
	685	770	1480	1570
0.05	-	0.3	-	0.4
0.10	-	0.4	-	0.6
0.20	0.4	1.8	0.8	1.4
0.30	1.4	3.2	1.8	2.4
0.50	3.2	6.4	3.5	4.6
1.00	5.4	14.2	6.4	12.0

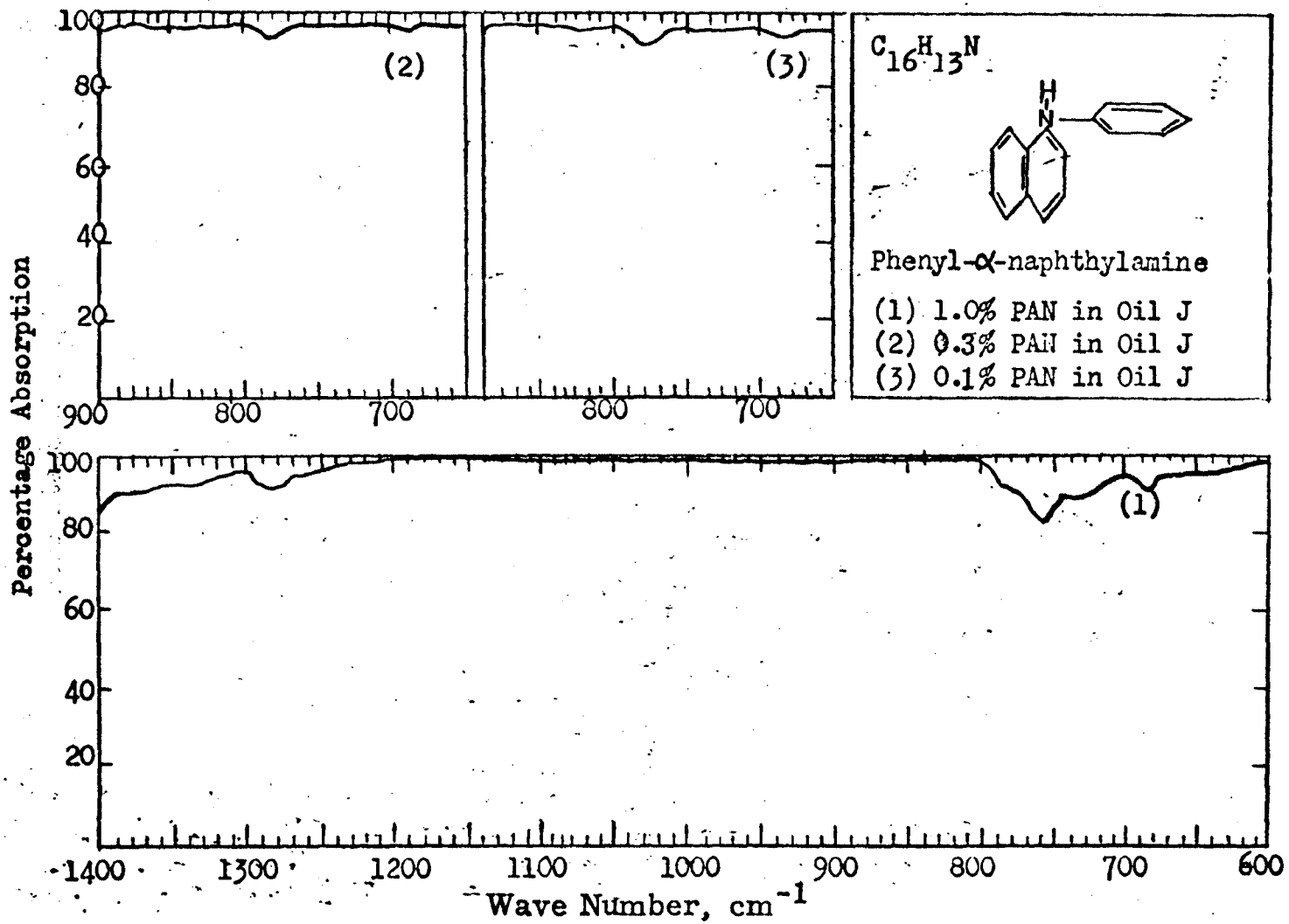

Figure 6. Portion of a Double Beam Projected IR Spectra

spectrophotometer which operates in the wavelength range of 2 to 16 microns.

Double beam(one pure oil, the other oil with additive) spectrophotometry was chosen for this analysis. This shows up the difference in the two solutions, i.e. the concentration of additive alone, and provides a quick and sensitive reading of the additive concentration which is represented by the absorbing bands.

Two NaCl crystals 0.1 mm apart form the slit which holds the film-type liquid sample. This pair of crystals is mounted on a stainless steel frame to form the complete sample cell.

At the start, the clearness of these two cells was checked visually, and a volatile solvent(benzene) was used to rinse away any foreign matter. After air drying, three drops of pure lubricant oil, the same as used in the extraction experiment, were inserted into the upper opening end of the sample cell with the help of a medicine dropper. A medical syringe was then mounted over this upper end opening. By pushing the rod down gently the oil flowed down the narrow slit and formed a 0.1 mm thick oil film through which the infrared beam was projected. Air bubbles had to be prevented from getting into this film. If bubbles were found, the procedure was repeated. Two pieces

of plastic end sealings were then carefully squeezed into the ends of the cell. This ensured that the oil film remained in position without any further disturbance throughout the experiment. The additive sample was charged to the solution cell in the same way as the pure solvent.

Each standard sample was scanned with the infrared light beam three times on the same piece of graph paper to get three corresponding curves, one for double beam, one for solvent single beam, and the other single beam for additive solution. For the absorption and extraction experimental samples, only one projection was made using the double beam for reading convenience. Calibration was accomplished by running a standard additive solution in the expected concentration range before each set of analyses. Peak heights were then compared using a procedure known as base line analysis(see Figure 7). In this technique a base line is drawn tangent to the local minima on either side of the peak. The distance between the peak and the base line is proportional to the magnitude of the percent absorbance of the additive at that particular wave length. Thus by measuring the absorbing bands for a functional group at different concentrations of additive(0.05%, 0.1%, 0.2%, 0.3%, 0.5%, 1.0%, and 1.38%), a set of peak heights versus concentrations of additive data could

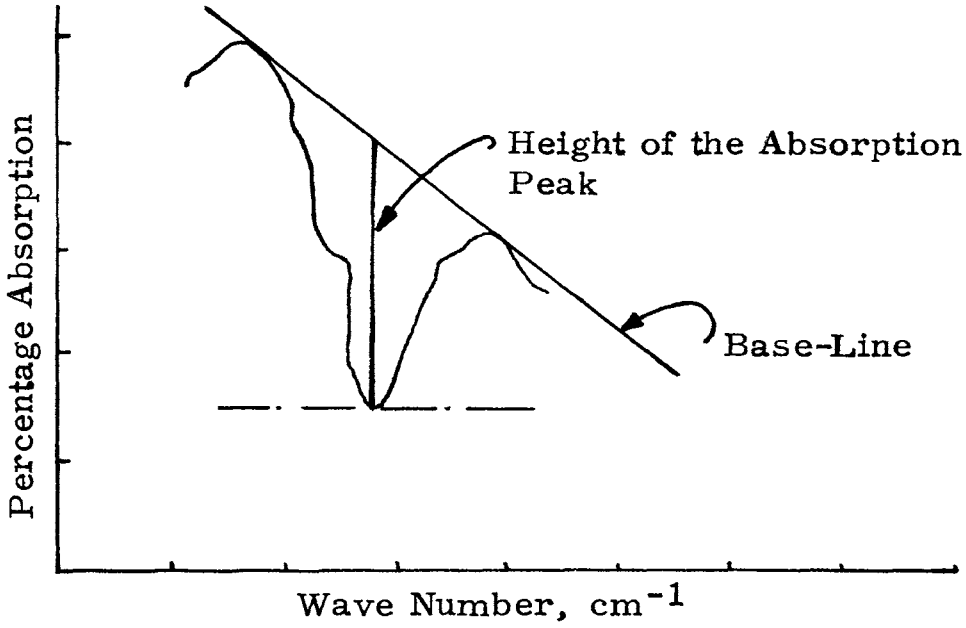

Figure 7. Illustration of the Base-Line Method

be tabulated(TableII). Because of fluctuations in peak heights from day to day standard samples were run each time analyses were made. By comparing a solution with an unknown percentage of the same additive with these calibration curves, a quantitative analysis of the unknown was obtained.

2. Grease Analysis

Grease samples from additive absorption and extraction experiments were carefully taken out of the permeability apparatus after the run was over.

Samples for infrared analysis were taken from different positions of each grease sample, i.e. from the top center, bottom center, top outer, and bottom outer parts. Each sample was carefully divided and cut with a small spatula, and transferred to the inside bottom of a syringe. The syringe was, in turn, mounted on one end of the IR sample cell holder. By pushing the syringe rod down hard but slowly, the grease was forced into the IR test cell. The grease sample without additives from which the sample grease was made was used as the reference for the double beam analysis.

In the case of the LOA run, analyses of the top center, bottom center, top outer, and bottom outer gave 0.98%, 0.95%, 0.98% and 0.92% additive, respectively. Thus, the additive appeared to

be uniformly distributed throughout the grease.

Samples taken from the same locations from the BOA run all contained about 1.65 % additive. However, a grease sample scraped off the bottom of the top filter paper (estimated to be about 1/20 of the sample thickness) contained 4.0% of additive. The filter paper was considerably darker than the rest of the greases at the end of the run, and absorption of additive on the paper was probably the cause. This was not observed to be as pronounced in LOA, probably because the total run time was only 339 hours compared with 615 hours for BOA.

For LGA and BGA, samples were taken from the top and bottom of the entire grease cakes, and no significant differences were observed. The results were 0.20 and 0.25% additive, respectively.

IV. RESULTS AND DISCUSSION

A. Permeability Experiments

The results of the permeability tests are listed in Tables III and IV and shown in Figures 8 and 9. Repeatability was quite good. The maximum range of deviations from the average for three runs was ±3%.

1. Lithium-Calcium Greases

For the lithium-calcium greases made with naphthenic oils, the permeability coefficients increased from 3.8×10^{-11} to 10.0×10^{-11} cm^2 as the viscosity of the oils from which the greases were made increased from 117 to 2450 centistokes at 70°F. For the paraffinic oil series, the viscosity range was limited to 108 to 680 centistokes. Over the same range of oil viscosity, the permeability coefficients varied less with paraffinic oils than with naphthenic oils.

The grease made with the solvent refined naphthenic oil, which is similar to oils used commercially in many multi-purpose greases, had the lowest permeability coefficient, 3.0×10^{-11} cm^2. The grease made from the paraffinic Pennsylvania base oil had a permeability coefficient close to that of the solvent refined paraffinic oil of about the same viscosity and VI.

TABLE III

Summary of Permeability Results for Lithium-Calcium Stearate Greases

Grease	Viscosity, cs (at 70°F)	Value of K (x 10^5)	Slope (x 10^6)	Permeability (x 10^{11})	Average
LA	117	0.956	4.0	3.8	
			4.0	3.8	3.8
			4.1	3.9	
LB	345	2.82	2.3	6.4	
			2.4	6.6	6.5
			2.3	6.5	
LD	2450	20.95	0.48	10.0	
			0.48	10.0	10.0
			0.48	10.0	
LE	108	0.884	10.3	9.1	
			10.6	9.3	9.2
			10.5	9.3	
LF	330	2.70	2.3	6.2	
			2.3	6.2	6.3
			2.4	6.4	
LG	680	5.56	1.20	6.6	
			1.25	6.8	6.7
			1.20	6.7	
LJ	320	2.62	1.15	3.0	
			1.15	3.0	3.0
			1.20	3.1	
LK	320	2.62	2.8	7.4	
			2.8	7.4	7.5
			2.9	7.7	

TABLE IV

Summary of Permeability Results for Baragel Greases

Grease	Viscosity, cs (at 70°F)	Value of K (x 10^5)	Slope (x 10^6)	Permeability (x 10^{11})	Average
BA	117	0.956	2.5	2.4	
			2.4	2.3	2.3
			2.4	2.3	
BB	345	2.82	1.39	3.9	
			1.43	4.0	4.0
			1.46	4.1	
BC	880	7.20	0.80	5.7	
			0.80	5.8	5.9
			0.84	6.0	
BD	2450	20.95	0.49	10.2	
			0.51	10.5	10.4
			0.55	11.4	
BE	108	0.88	11.8	10.4	
			11.6	10.2	10.3
			11.7	10.3	
BF	330	2.70	3.1	8.3	
			3.2	8.6	8.5
			3.2	8.6	
BG	680	5.56	1.46	8.1	
			1.53	8.5	8.3
			1.48	8.3	
BH	1850	15.15	0.70	10.6	
			0.69	10.5	10.3
			0.66	10.0	
BJ	320	2.62	1.42	3.7	
			1.45	3.8	3.8
			1.49	3.9	
BK	320	2.62	3.1	8.2	
			3.0	7.9	8.0
			3.0	8.0	

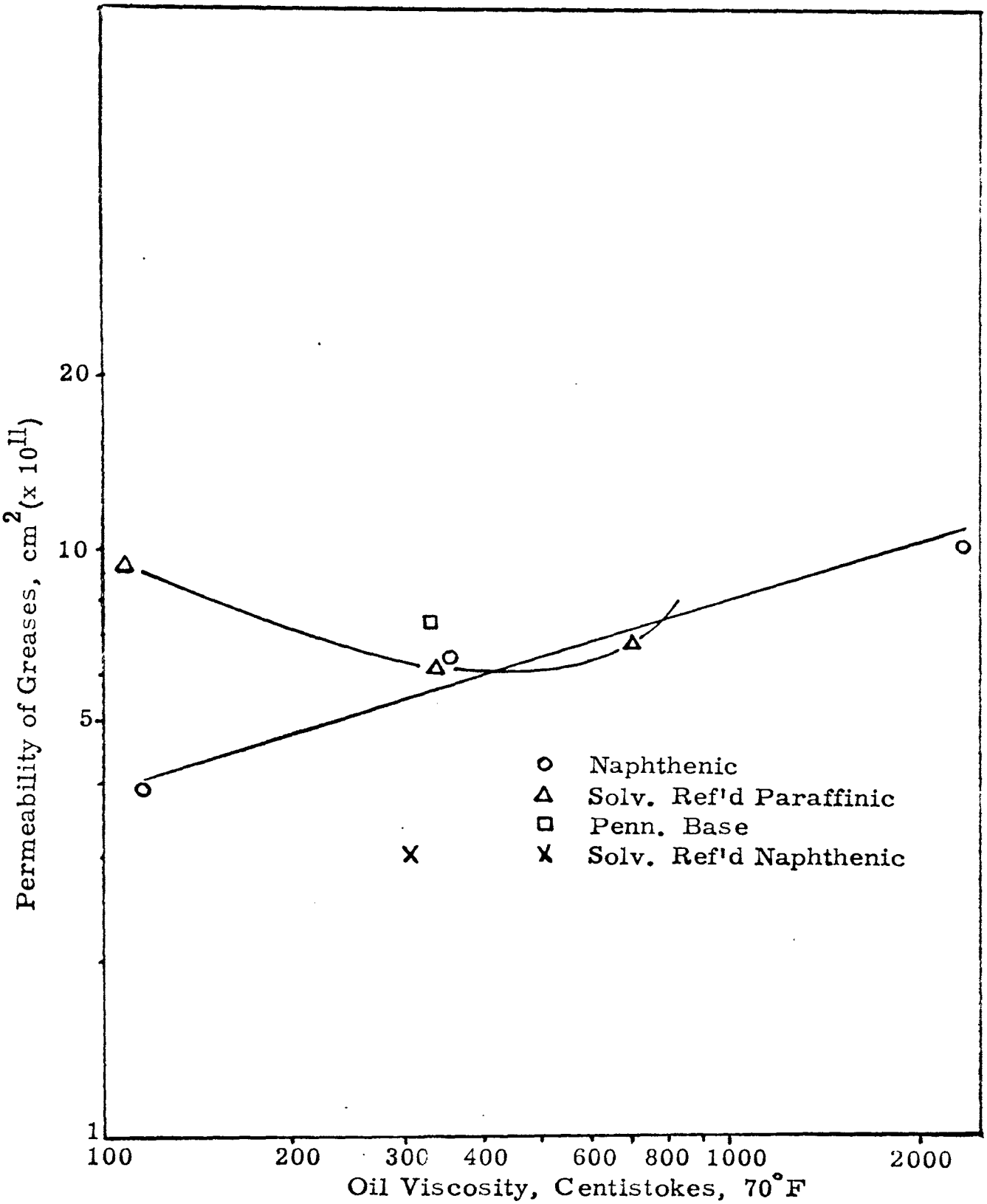

Figure 8. Permeability vs. Oil Viscosity for Lithium-Calcium Greases

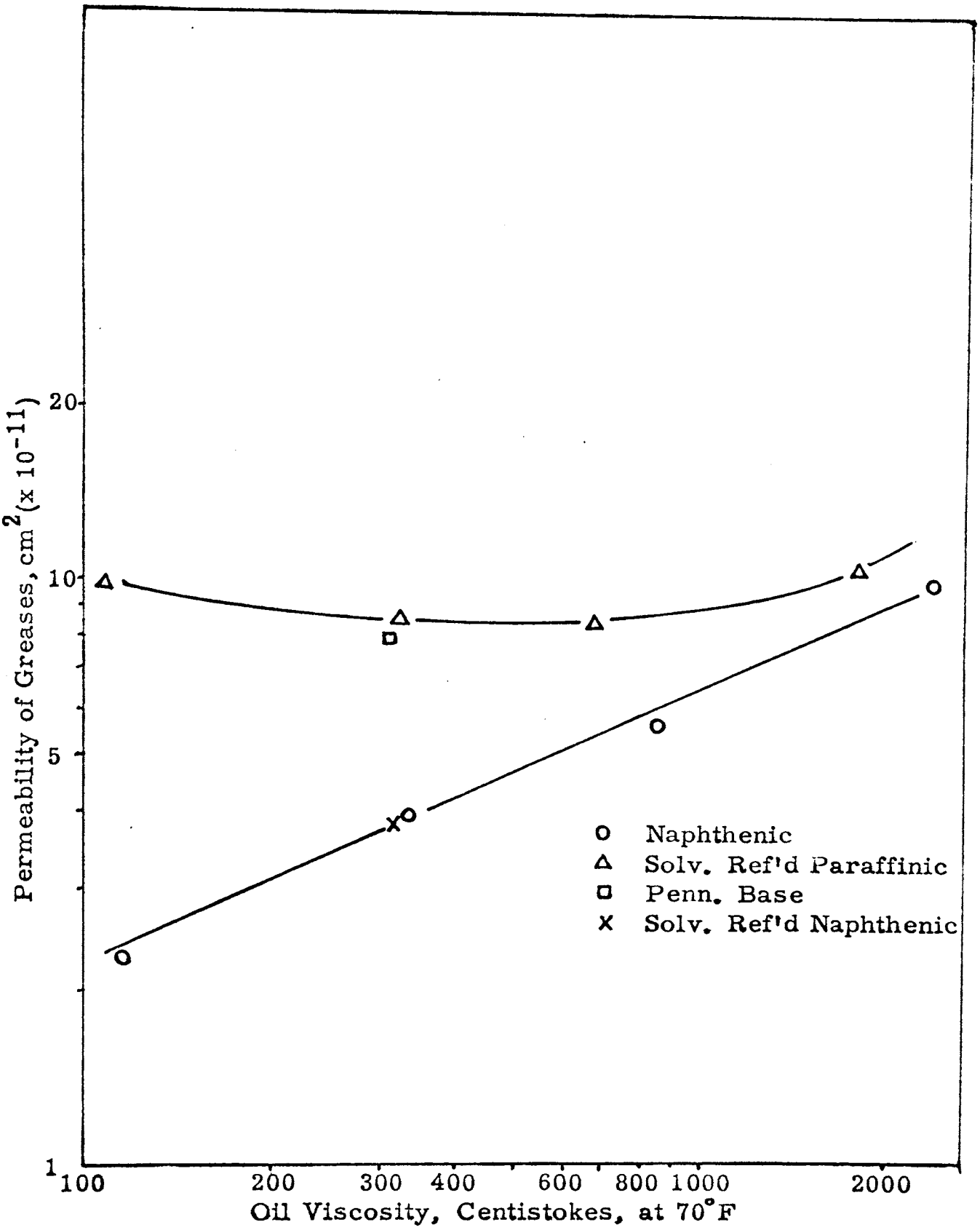

Figure 9. Permeability vs. Oil Viscosity for Baragel Greases

Based on initial rates of oil separation in pressure separability and in cone bleeding tests(10) and on these permeability test results on the naphthenic oil series, the lithium-calcium soap appears to be more dispersed and the structure more resistant to oil permeation when formed in a low viscosity oil environment and less dispersed and less resistant when formed in a high viscosity oil environment. Panzer(8) has stated that an increase in particle size(less dispersed) can be expected as viscosity increases if the reaction time is long enough.

However, the small variations in the permeability coefficients for the greases made with paraffinic oils of widely different viscosities is not consistent with the initial rates of oil separation in either the pressure separability or the cone bleeding tests reported earlier(10). Thus, for paraffinic oils, there is a question as to which, if any, of these three test procedures gives a true measure of thickener dispersion. Data on other types of greases and perhaps electron micrographs showing details of the grease structure for all of the greases studied are needed to resolve this question.

2. Baragel Greases

The permeability coefficients of the Baragel greases made with naphthenic oils increased from 2.3 to 10.4 x 10^{-11} cm^2 as

viscosity varied from 117 to 2450 centistokes at the test temperature(70 °F). The grease made from the solvent refined naphthenic oil has a permeability coefficient which lies close to the curve for the naphthenic series. The characteristics of the solvent refined naphthenic oil which led to a very low permeability coefficient for the lithium-calcium grease, gave no special effects with Baragel. The increase in the permeability coefficient with viscosity of the oil in this naphthenic series probably reflects poorer dispersion of the Baragel thickener at the higher viscosities.

The permeability coefficients of the greases made with paraffinic oils ranged from 8.3 to 10.4 x 10^{-11} cm^2 when oil viscosity was varied from 108 to 1850 centistokes at 70 °F. Thus, for the paraffinic series, the degree of dispersion of the Baragel appears to be relatively insensitive to the oil viscosity environment in which the thickener structure was formed. The Pennsylvania paraffinic oil blend has a permeability coefficient slightly lower than the paraffinic oil of similar viscosity and VI.

B. Extraction and Absorption Experiments

1. Extraction.

The results of the additive extraction experiments for greases LGA and BGA are given in Tables V and VI and are plotted in Figures 12-15. Initial additive concentration in both samples was 1.38%.

Equilibrium concentrations of PAN additive in the grease were reached after about 25 cc of extract oil had passed through the 7.4 cc grease sample in the case of LGA and about 35 cc for BGA. The equilibrium concentrations of PAN in the greases in contact with pure oil were 0.18% for LGA and 0.23% for BGA. These values were calculated from mass balances as shown in Appendix A-2. Infrared analyses of the greases gave values of 0.20% and 0.25%.

From these results it is not possible to determine whether the additive is initially dissolved in oil throughout the grease structure or whether it is absorbed on the thickener surface or whether a combination of both occurred. Previous estimates of the non-recoverable oil in different greases are from 65-95%(10) to 78%(15), but in both cases the estimates are from indirect methods and are subject to considerable error. The non-recoverable oil is presumably trapped in isolated pockets in the

grease structure.

If we assume that:

1. additive dissolved in oil trapped in pockets is also trapped.

2. at least 50% of the oil is trapped.

then the hypothesis that the additive is uniformly dispersed throughout the oil phase can not account for the low final concentrations that were found, as more than half of the initial additive would have remained in the grease. On the contrary, it appears that a major portion of the additive had to be accessible to the extract oil. This implies that most or all of the additive was absorbed on the thickener surface initially and partially or totally removed during the extraction.

In those parts of the discussion in which the non-equilibrium portions of the runs are considered, average concentrations for the grease samples were used. Although the test samples had a high surface to thickness ratio the assumed uniformity can not truly exist. Nevertheless the assumption is useful for qualitative comparisons of the data.

The results are also plotted in the form of log (% additive in grease at any stage - final equilibrium % additive) / (% additive at start of test - final equilibrium % additive) versus (volume of extract oil / volume of grease sample) or Y versus X in Figure 10. The dimensionless ordinate, Y, measures the fraction of

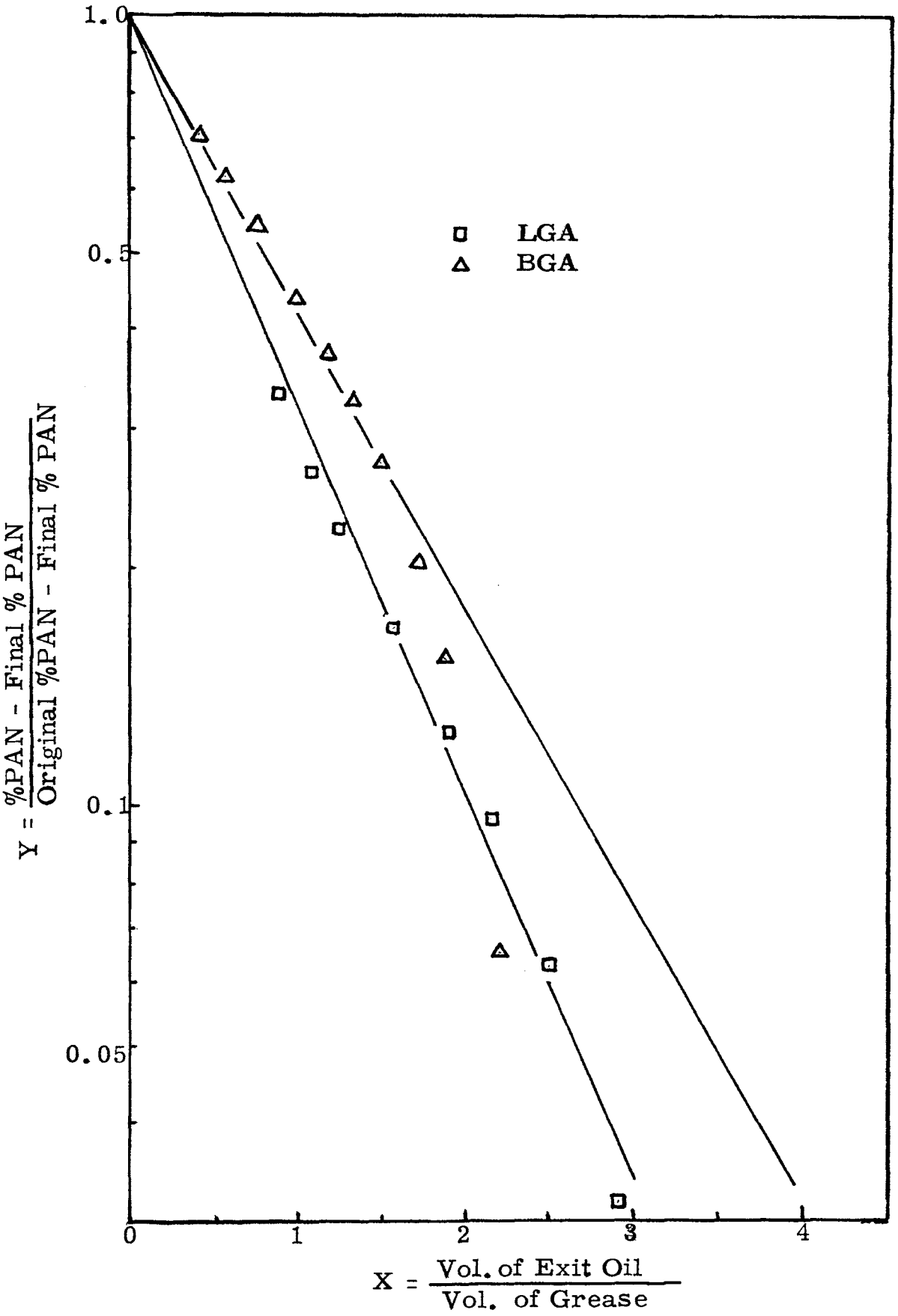

Figure 10. Reduced Plot of Fraction of Additive Removed vs. Extract Oil Volume for LGA and BGA

the removable additive present and is shown as a function of the volume ratio of extract oil, X.

For both the lithium (LGA) and Baragel (BGA) greases, the semilogarithmic plot is linear with negative slopes at the start of the runs and then steepens at higher values of X, about 2.5 for LGA and 1.5 for BGA. The initial slopes are - 0.49 and - 0.37, respectively. In the linear region, the data appear to follow the equation $Y = e^{-kx}$ where k is the absolute numerical value of the slope. The function does not fit the data as the process of extraction approaches equilibrium.

The lower slope of the Baragel run means that the rate of approach to equilibrium in removal of additive from the grease is lower than for the lithium grease during the early stages of extraction. Since the initial and final concentrations of PAN for both greases are about the same, we can also compare Figures 12 and 14. Here the absolute rate of PAN extraction is greater for LGA than for BGA up to about 20 cc of extract oil.

The deviations at high values of X may be due to experimental error in determining additive concentration, the importance of which increases as concentration falls, as the numerator of Y becomes the small difference between two relatively large numbers and a small error in either will

have an important effect on the difference.

2. Absorption.

The results of the additive absorption experiments for greases LOA and BOA are given in Tables VII and VIII and the results are plotted in Figures 16-19.

Equilibrium concentrations of PAN additive in the greases in equilibrium with 1.0% of additive in the oil were reached after about 25 cc of permeated oil had passed through LOA and 50 cc through BOA. The equilibrium concentrations of PAN in the greases were 0.90% for LOA and 1.79% for BOA calculated from mass balances of additive in the permeating oil. Calculations are shown in Appendix A-3. Infrared analyses of the greases gave values of about 0.96% and 1.65%. Some error was introduced into the BOA calculation because a part of the additive was absorbed on the filter paper (see Experimental D-2).

The large value of the final BOA equilibrium concentration indicates that considerable PAN additive is absorbed and held on the thickener surface. Since only a fraction of the original oil containing no additive can be replaced, and at equilibrium the oil which has replaced it should have an additive concen-

tration close to 1.0%, much of the equilibrium amount of additive in LOA must also be absorbed on the thickener surface to account for the 0.90% final concentration.

In addition, plots of the form 1 - (% additive in grease / final equilibrium % additive) versus (volume of extract oil / volume of grease sample) or Z versus X are shown in Figure 11. The dimensionless ordinate Z measures the approach to equilibrium, small values of Z indicating near equilibrium conditions.

For both the lithium and the Baragel greases, the semi-logarithmic plot is linear with negative slopes at the start of the runs which steepen at higher values of X (about X = 1.5 for LOA and about X = 2.0 for BOA). The initial slopes are - 0.46 and - 0.20, respectively. The data appear to follow the equation $Z = e^{-kx}$, where k is the absolute numerical value of the slope.

The steeper curve for the lithium grease means a more rapid approach to equilibrium than for the Baragel grease. Since the lithium grease final equilibrium concentration was only 0.90% while the Baragel grease concentration was 1.79%, this difference in slopes represents the longer time required to build up this higher concentration. Figures 16 and 18 show that the initial absolute rate of concentration build-up in LOA

is about the same as in BOA.

The previous explanation for the deviations at high values of X applies here also. In this region, the value of Z is the difference between two large, nearly equal numbers and is very sensitive to an error in analysis.

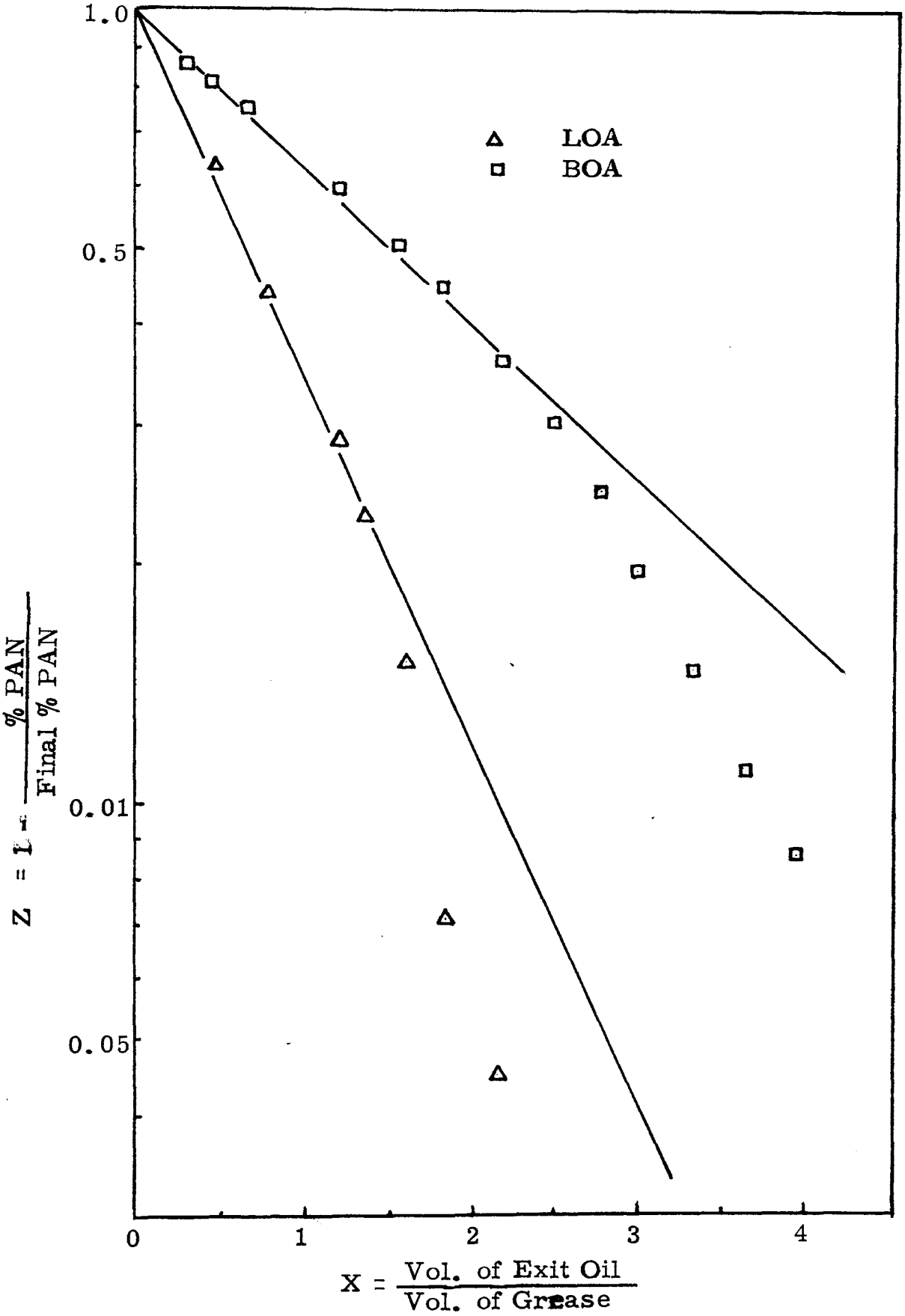

Figure 11. Reduced Plot Relating Fraction of Additive Absorbed vs. Volume of Permeating Oil for LOA and BOA

V. RECOMMENDATIONS FOR FUTURE WORK

I. Permeability Measurements.

1). A systematic study of many systems using the variables of viscosity, oil composition, and nature of grease thickener should be made. The viscosity range may be extended to cover a wider range.

2). Variation of temperature may be used to determine the effect of temperature on permeability and to establish the limits at which the temperature starts to affect the permeability significantly.

II. Extraction and Absorption Measurements.

1). Vary the percent of PAN in oil in absorption experiments. to obtain equilibrium concentration curves.

2). Check reversibility of experiments by extracting additive after completion of additive absorption test. Also check the effect of re-adding additive after an extraction test. The final equilibrium concentrations obtained may give further insight into the question of whether the additive is entirely absorbed on the thickener surface or partially trapped in isolated pockets of the thickener structure.

3). Check uniformity of additive in grease sample at all stages of test. Redesign sample cell to increase sample height to facilitate this study.

4). Investigate path of additive flow through grease cake.

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VII. APPENDICES

A. Sample Calculations

1. Permeability Coefficient Calculation

A complete sample calculation of the permeability coefficient of one grease based on Darcy's Law is shown below:

Baragel grease Run BG-3:

viscosity of the oil blend: 680 centistokes at 70°F

area of pipette: $A_p = 0.2623\ cm^2$

area of grease sample: $A_s = 15.55\ cm^2$

ratio of $A_p/A_s = 0.01685$

sample thickness: 0.476 cm

(figures of slope calculation were interpolated from the smooth curve of Run BG-3):

slope of the curve: $\frac{d\ ln(h)}{dt} = \frac{(\log 27.7 - \log 20.25) \times 2.303}{(59. - 2) \times 3600}$

$= 1.48 \times 10^{-6}\ sec^{-1}$

$$K = \frac{\nu L A_p/A_s}{g}$$

$$= \frac{(680 \times 10^{-2})(0.476)(0.01685)}{980.66}$$

$= 5.56 \times 10^{-5}\ cm^2 - sec$

$B = (5.56 \times 10^{-5}) \times (1.48 \times 10^{-6})$

$B = 8.3 \times 10^{-11}\ cm^2$

This is the calculated permeability coefficient of grease BG

including the screens, filters and the grease sample.

Corrections for the resistance of the screens and filters should be made to obtain the permeability of the grease.

Using the sample equation as shown above and by running a blank experiment with the same screens and filters but no grease sample and with the same oil(see Table XXVII), B_o is,

$$B_o = 5.56 \times 10^{-5} \times \frac{\log(29.1/10.2)}{(45 - 0) \times 60} = 9.5 \times 10^{-9} \text{ cm}^2$$

the permeability coefficient of the screens and filters only. The total resistance is the sum of the individual resistances

$$\frac{1}{B} = \frac{1}{B_o} + \frac{1}{B_c}$$

Where B_o is the total permeability of the grease sample with screens and filters and B_c is the permeability of the grease itself after correction.

$$B_c = \frac{B \times B_o}{B_o - B}$$

$$= \frac{(3.7 \times 10^{-11}) \times (9.5 \times 10^{-9})}{9.5 \times 10^{-9} - 3.7 \times 10^{-11}}$$

$$= 3.7 \times 10^{-11} \text{ cm}^2$$

The correction of the apparatus resistances in this case is of negligible importance. This is true of all samples studied, and corrections were not made.

2. Calculation of Additive Remaining in Greases LGA and BGA, After Extraction with Pure Oil.

Area of the grease sample: 15.55 cm^2

Height of the sample: 0.476 cm

Volume of the sample: 15.55 x 0.476 = 7.40 cm^3

Density of both greases: 0.90 gm/cc

Density of the oil: 0.90 gm/cc

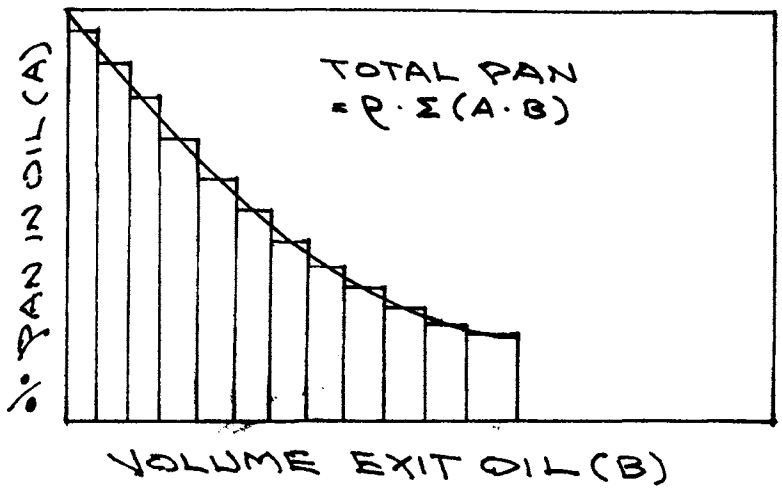
Weight of the sample: 7.40 x 0.90 = 6.66 gm

Weight of the PAN additive in the grease sample: 1.38%

Total PAN in the sample: 6.66 x 1.38% = 0.092 gm

LGA:

Total additive removed from the grease(integration of the area under the curve of % additive in oil versus volume of exit oil multiplied by density, see sketch): 0.089 x 0.90 = 0.80 gm



Final additive remaining in the grease sample: 0.012 gm

Calculated percent of additive in the grease sample, LGA:

$$\frac{0.012 \times 100}{6.66} = 0.18\%$$

Average percent additive in the grease sample by IR analysis: 0.20%

BGA ;

Total additive removed from the grease(integration of the area under the curve of % additive in oil versus volume of exit oil of BGA multiplied by density, see sketch on p. 62):

$0.086 \times 0.90 = 0.077$ gm

Final additive remaining in the grease sample: 0.015 gm

Calculated percent of additive in the grease sample BGA:

$$\frac{0.015 \times 100}{6.66} = 0.23\%$$

Average percent additive in the sample by IR analysis: 0.25%

3. Calculation of Additive Absorbed by Greases LOA and BOA.

LOA:

Total additive in the oil(38.5 cc with 1.0% PAN):

35.8 x 0.90 x 0.01 = 0.322 gm

Total additive remaining in the exit oil after passing oil with 1.0% additive through the LOA grease(integrating the area under the curve of % additive in oil versus volume of exit oil multiplied by density, see sketch on p. 62):

0.291 x 0.90 = 0.262 gm

Total additive retained in the grease: 0.060 gm

Calculated percent additive in LOA sample:

$$\frac{0.060 \times 100}{6.66} = 0.90\%$$

Average percent additive in LOA sample by IR analysis:

0.96%

BOA:

Total additive in the oil(52.5 cc with 1.0% PAN):

52.5 x 0.90 x 0.01 = 0.472 gm

Total additive remaining in the exit oil after passing oil with 1.0% additive through the grease(integrating the area under the curve of % additive in oil versus volume of exit oil for BOA

and multiplied by density, see sketch on p. 62):

0.392 x 0.90 = 0.352 gm

Total additive retained in the grease: 0.120 gm

Calculated percent additive in LOA sample:

$$\frac{0.120 \times 100}{6.66} = 1.79\%^{*}$$

Average percent additive in BOA sample by IR analysis:

1.65%*

* Absorption of additive on the filter paper surface can account for the difference in the additive extimates.

VII. APPENDIX

B. FIGURES

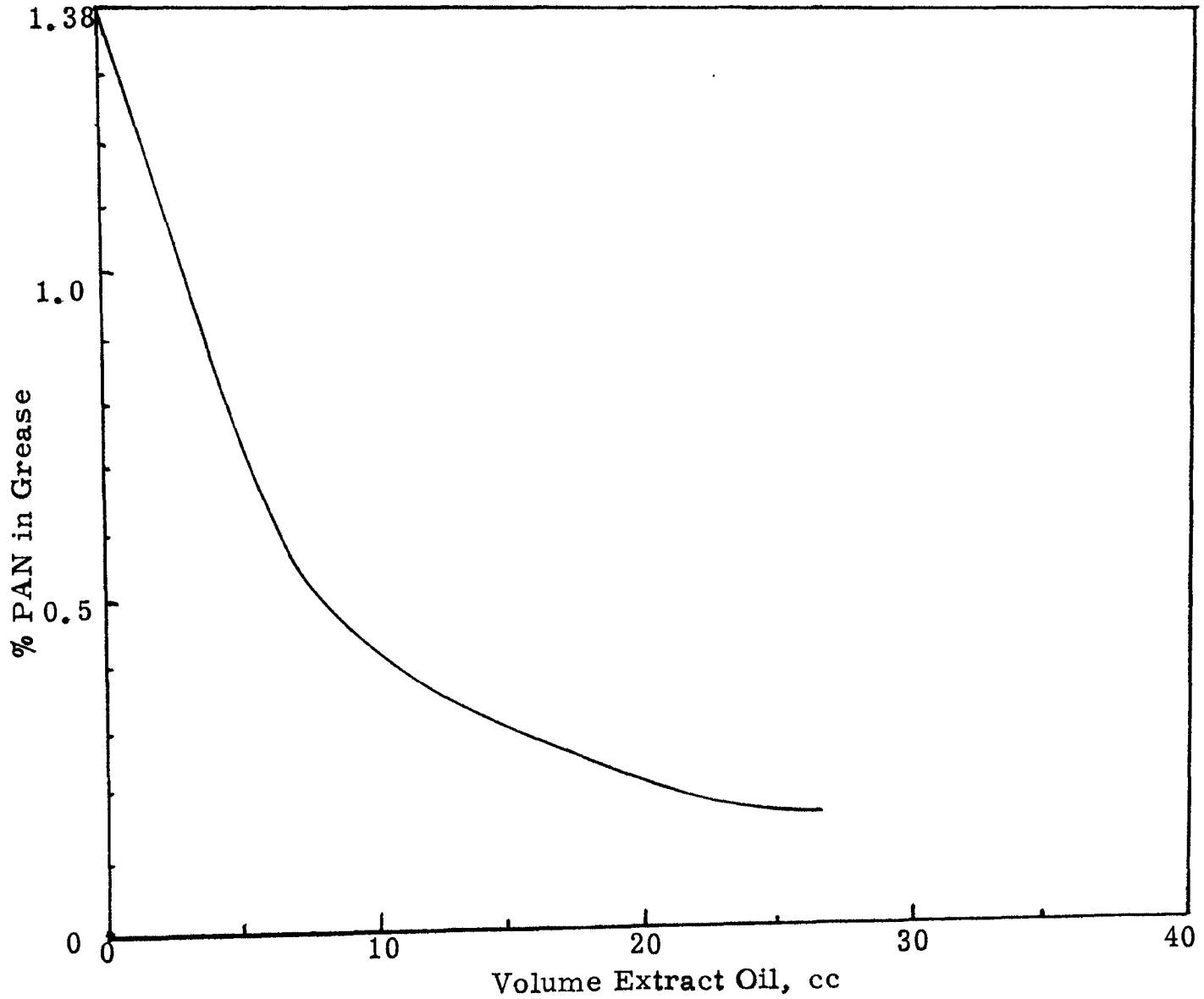


Figure 12. Effect of Volume of Extract Oil on %PAN in LGA

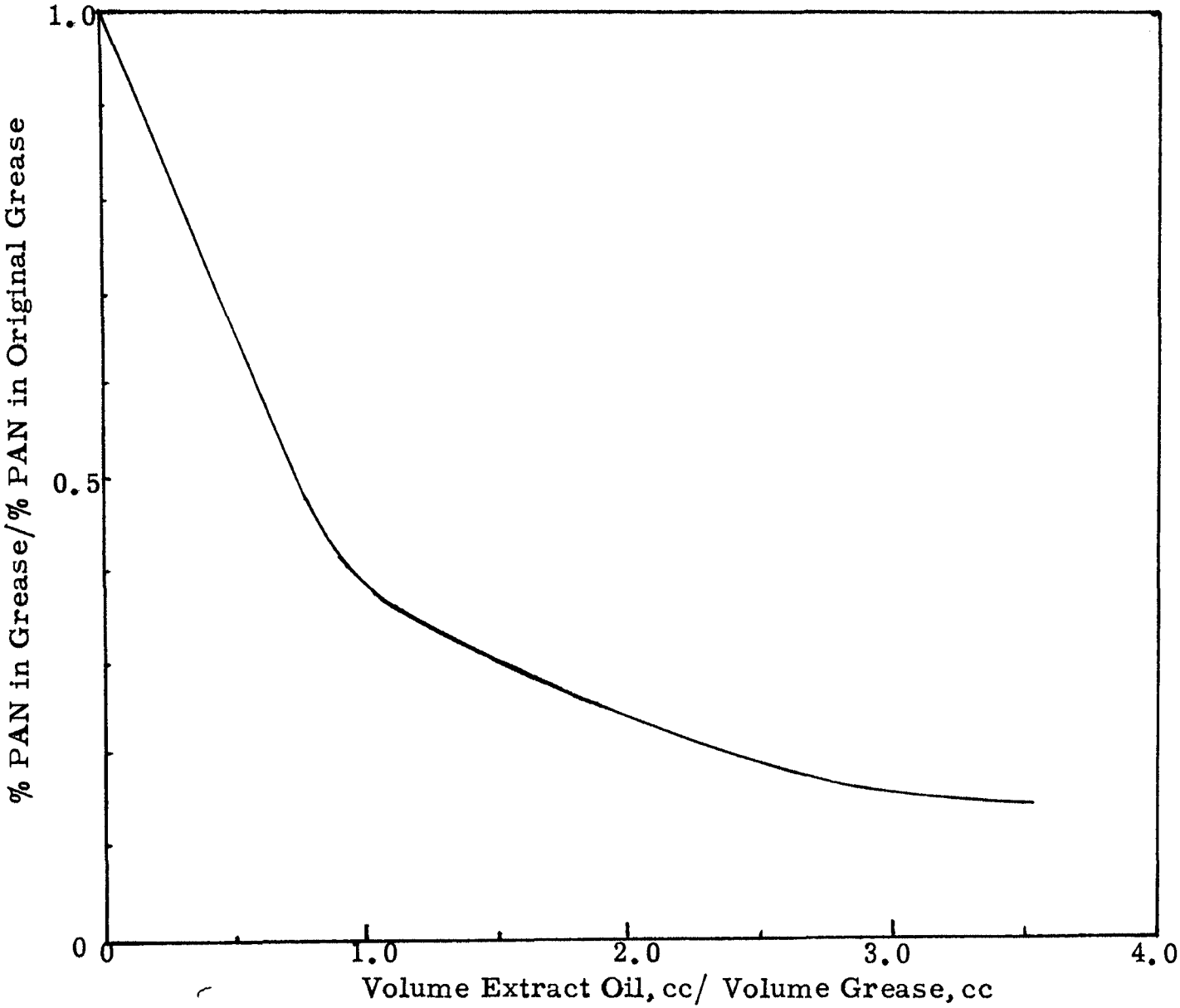


Figure 13. Reduced Plot of Effect of Volume of Extract Oil on %PAN in LGA

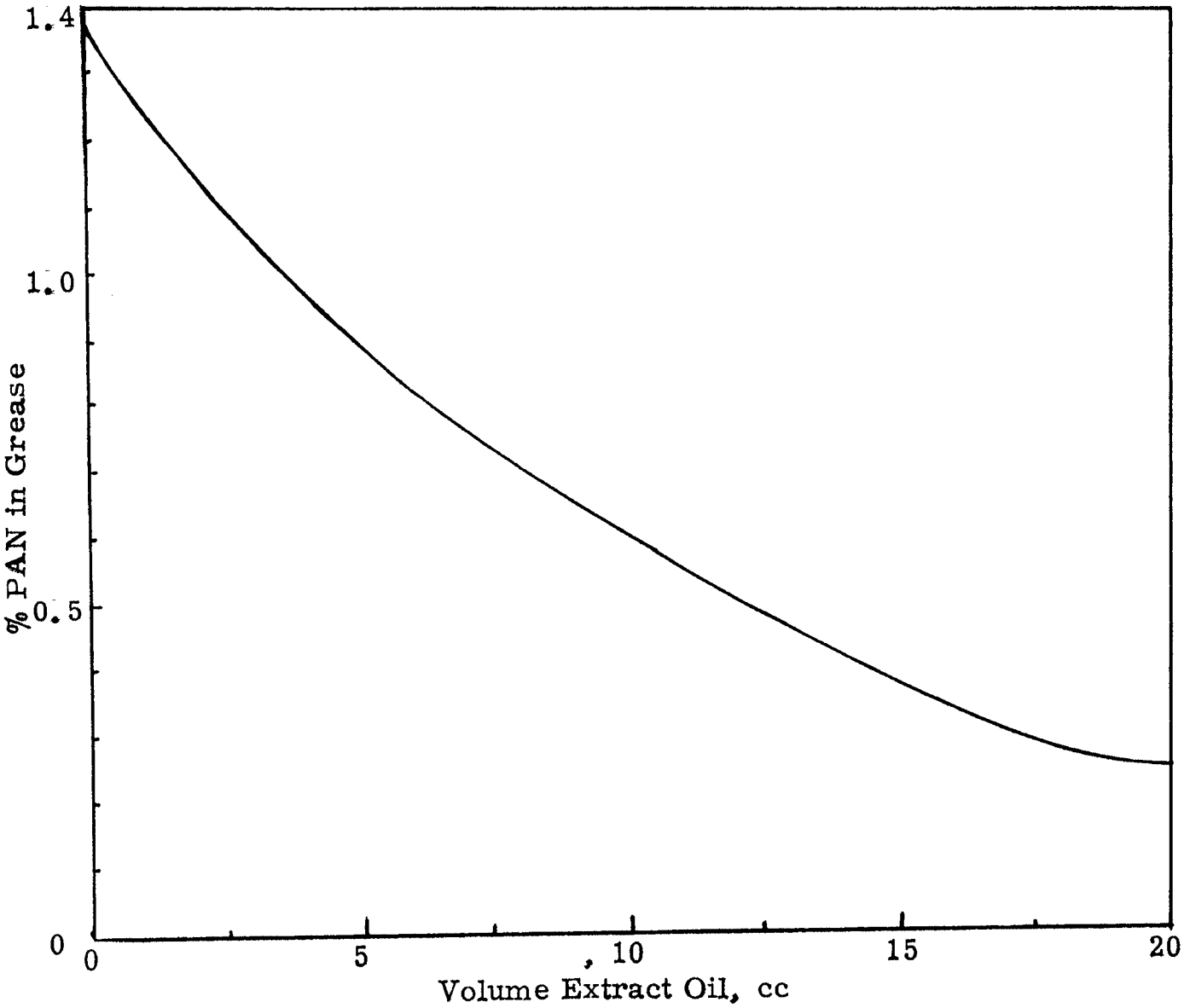


Figure 14. Effect of Volume of Extract Oil on % PAN in BGA

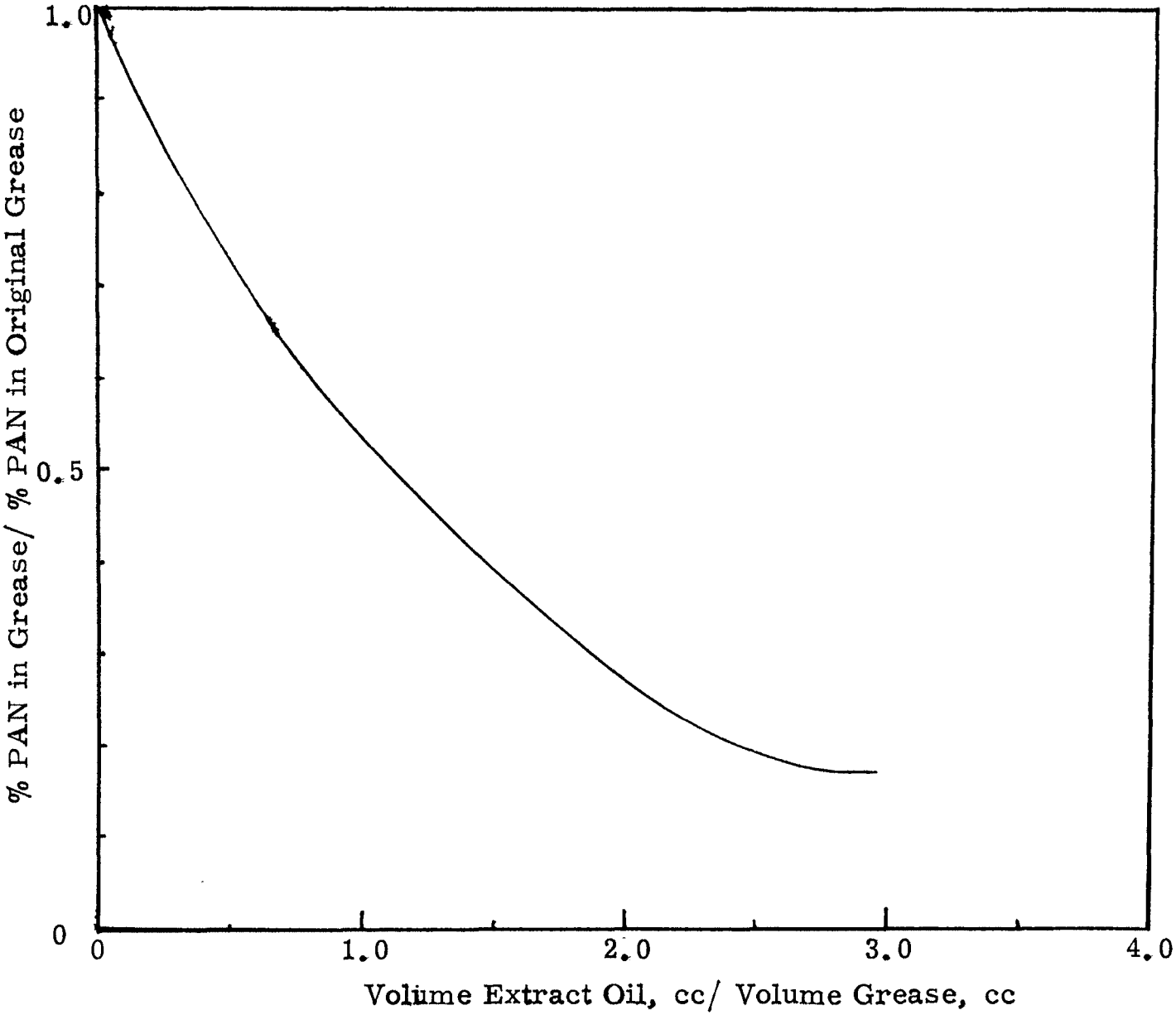


Figure 15. Reduced Plot of Effect of Volume of Extract Oil on %PAN in BGA

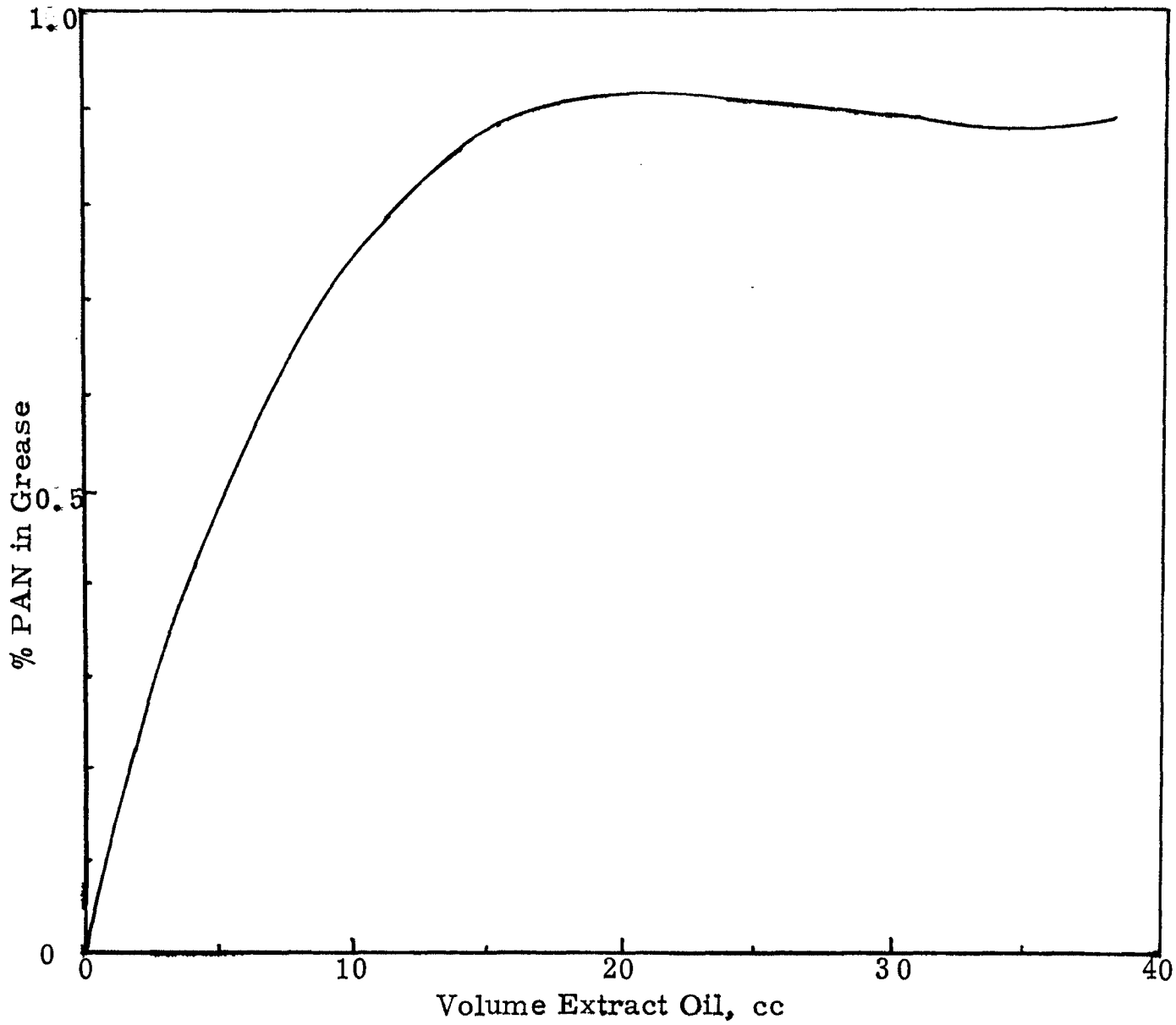


Figure 16. Effect of Volume of Oil Containing 1% PAN on %PAN in LOA

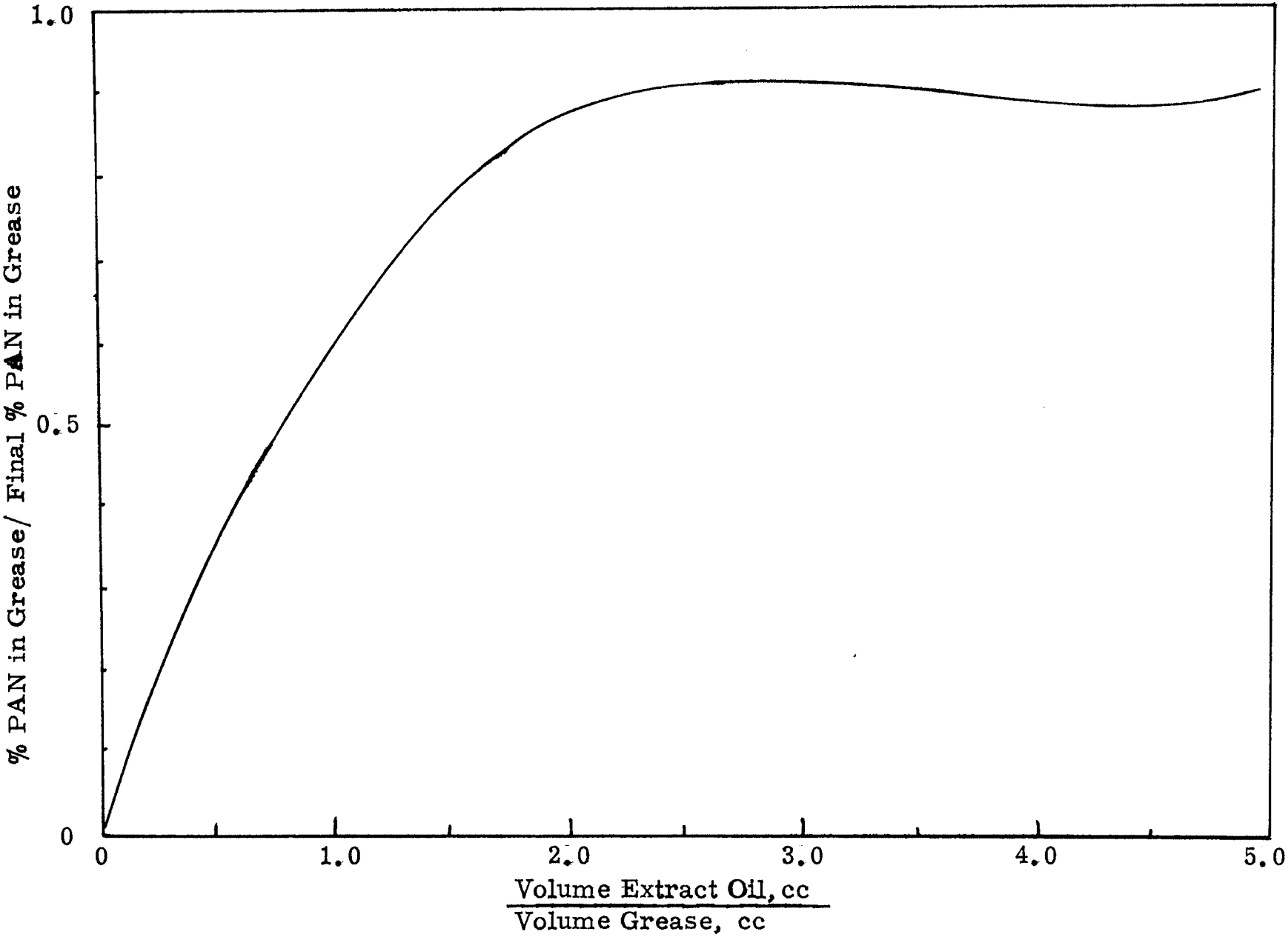


Figure 17. Reduced Plot of Effect of Volume of Oil Containing 1% PAN on %PAN in LOA

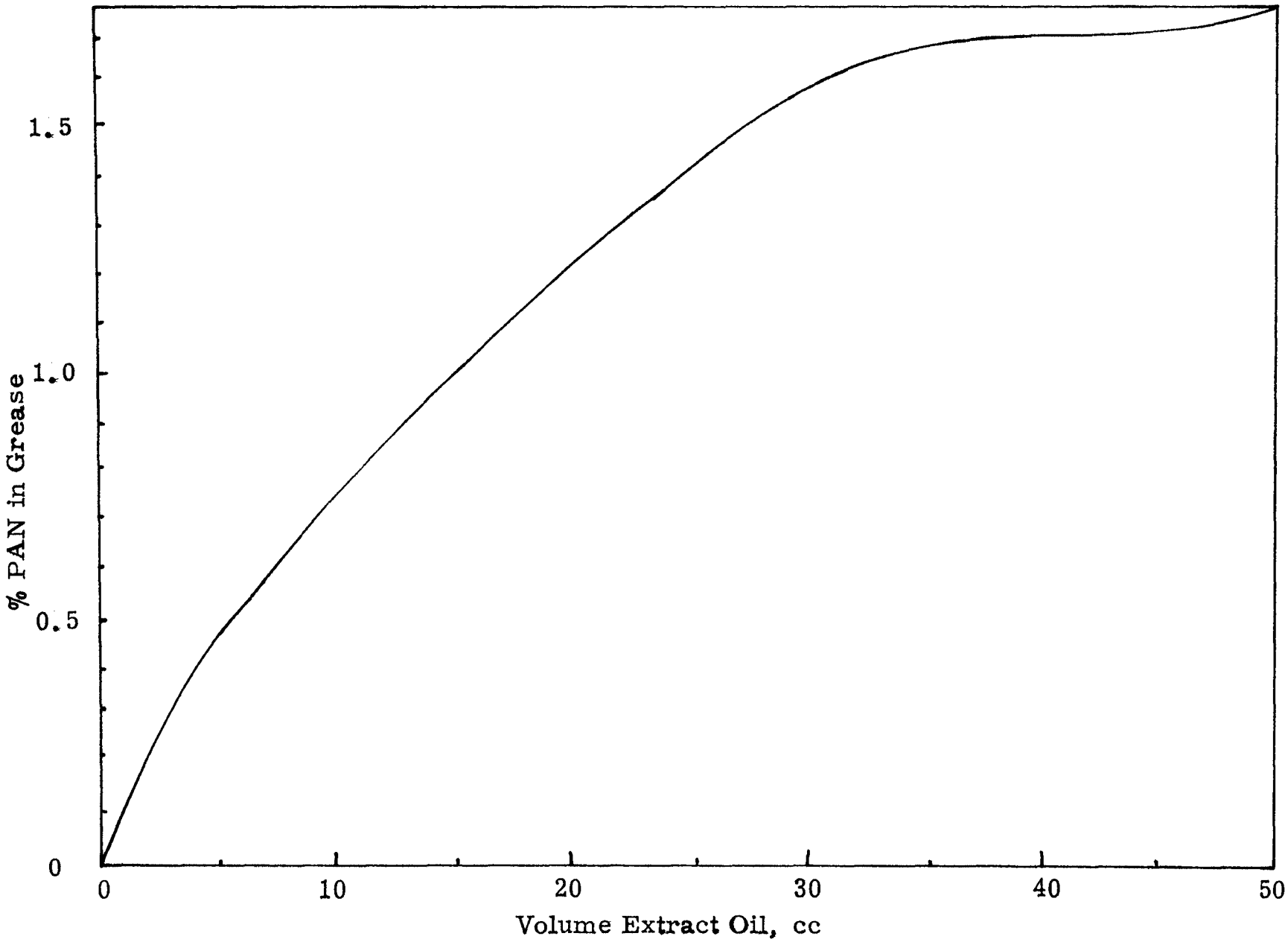


Figure 18. Effect of Volume of Oil Containing 1% PAN on % PAN in BOA

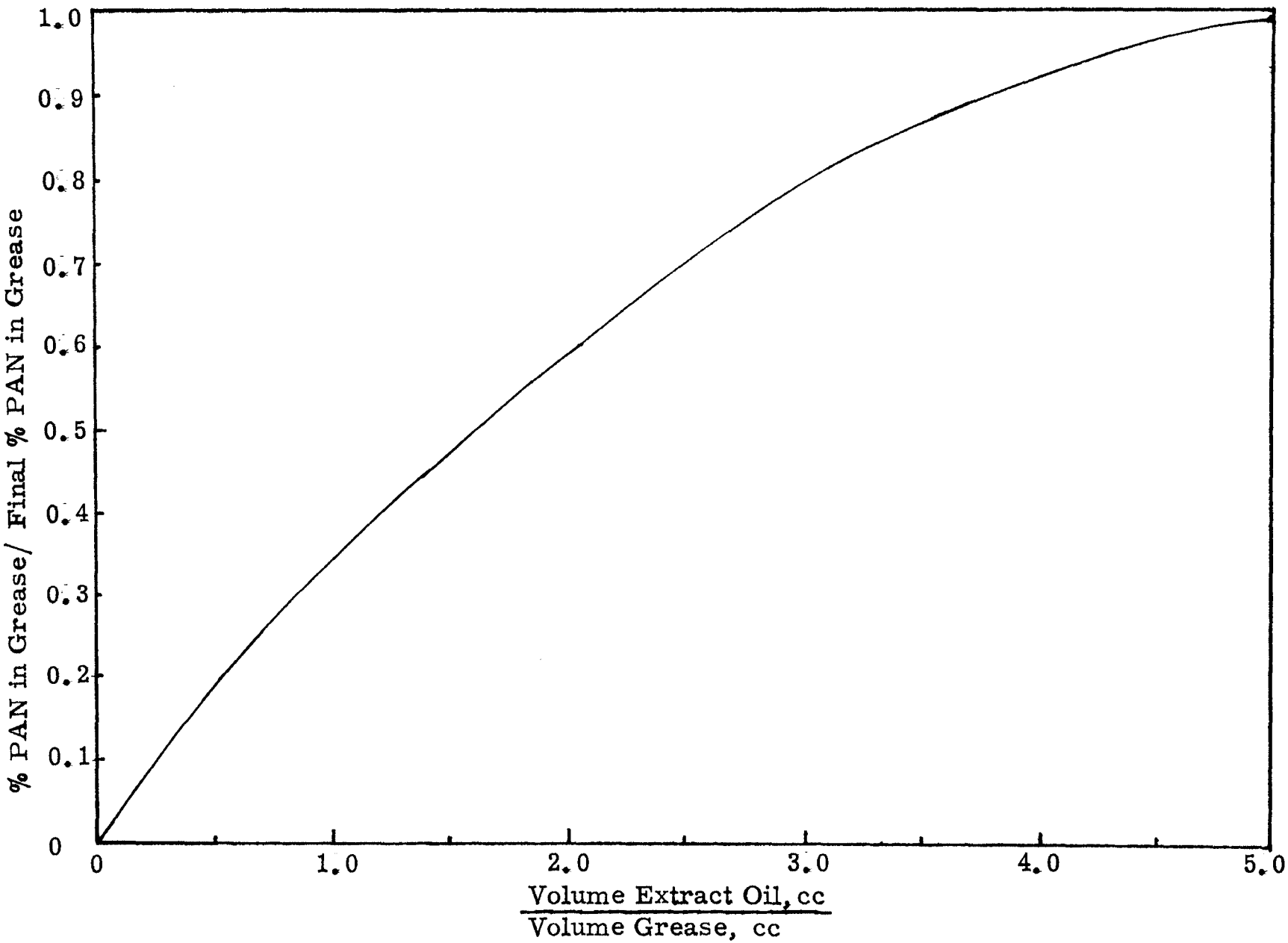


Figure 19. Reduced Plot of Effect of Volume of Oil Containing 1% PAN on %PAN in BOA

VII. APPENDIX

C. TABLES OF DATA

TABLE V

Extraction of Additive from Lithium Grease, LGA. Permeating Oil Contained No Additive, Initial Additive Concentration in Grease = 1.38%.

Sample No.	Hours	Volume cc	Volume Oil / Volume Sample	% Additive in Oil	% Additive in Grease
1	6	0.33	0.05	1.26	1.32
2	7.5	0.42	0.06	1.30	1.31
3	14	0.68	0.09	1.26	1.27
4	18	1.00	0.14	1.23	1.23
5	20.5	1.14	0.15	1.19	1.22
6	29	1.61	0.22	1.12	1.16
7	32	1.78	0.24	1.10	1.14
8	37	2.05	0.28	1.08	1.11
9	42	2.33	0.31	1.05	1.06
10	67	3.72	0.50	0.86	0.90
11	91	5.05	0.68	0.68	0.74
12	104	5.78	0.78	0.59	0.64
13	116	6.45	0.87	0.49	0.58
14	128	7.11	0.96	0.41	0.53
15	141	7.83	1.05	0.34	0.50
16	165	9.17	1.24	0.25	0.44
17	189	10.50	1.42	0.21	0.41
18	212	12.34	1.67	0.16	0.36
19	236	14.14	1.91	0.15	0.32
20	260	15.53	2.10	0.15	0.30
21	272	16.01	2.16	0.15	0.29
22	292	17.01	2.30	0.10	0.28
23	315	17.88	2.41	0.06	0.26
24	339	18.44	2.49	0.12	0.25
25	363	19.51	2.63	0.10	0.24
26	387	20.26	2.74	0.12	0.23
27	411	20.96	2.83	0.12	0.22
28	437	21.54	2.91	0.07	0.21
29	459	22.01	2.98	0.07	0.21
30	483	23.72	3.20	0.07	0.19
31	507	24.86	3.36	0.05	0.18
32	531	26.05	3.52	0.00	0.18
-					
33	579	28.61	3.87	0.00	0.18
34	600	30.11	3.98	0.00	0.18

TABLE VI

Extraction of Additive from Baragel Grease, BGA. Permeating Oil Contained No Additive, Initial Additive Concentration in Grease = 1.38%.

Sample No.	Hours	Volume cc	Volume Oil Volume Sample	% Additive in Oil	% Additive in Grease
1	27	1.34	0.18	0.60	1.21
2	36	2.46	0.33	0.70	1.10
3	49	2.89	0.39	0.70	1.06
4	65	3.96	0.54	0.59	0.96
5	76	4.50	0.61	0.56	0.92
6	90	5.41	0.73	0.50	0.85
7	105	6.16	0.83	0.42	0.80
8	117	6.68	0.90	0.39	0.78
9	130	7.21	0.98	0.45	0.74
10	141	7.72	1.04	0.42	0.71
11	153	8.14	1.10	0.40	0.69
12	165	8.57	1.16	0.39	0.67
13	177	9.13	1.23	0.39	0.64
14	189	9.78	1.32	0.37	0.61
15	217	11.04	1.49	0.34	0.54
16	231	12.04	1.63	0.34	0.50
17	255	12.74	1.72	0.34	0.47
18	275	13.36	1.81	0.33	0.43
19	299	13.94	1.88	0.32	0.41
20	323	14.54	1.97	0.30	0.39
21	345	15.09	2.04	0.28	0.36
22	366	15.82	2.14	0.28	0.33
23	384	16.48	2.23	0.26	0.30
24	404	17.14	2.32	0.24	0.29
25	416	17.74	2.40	0.22	0.27
26	441	18.57	2.51	0.17	0.25
27	450	19.17	2.59	0.12	0.24
28	469	19.71	2.67	0.00	0.23
29	492	20.22	2.74	0.00	0.23
30	516	20.74	2.80	0.00	0.23

TABLE VII

Absorption of Additive by Lithium Grease, LOA, Permeating Oil Contained 1.0 % PAN Additive.

Sample No.	Hours	Volume cc	Volume Oil Volume Sample	% Additive in Oil	% Additive in Grease
1	23	0.98	0.13	0.00	0.12
2	31	1.98	0.27	0.24	0.22
3	45	3.23	0.44	0.48	0.34
4	64	5.65	0.76	0.54	0.52
5	73	6.12	0.83	0.57	0.54
6	87	7.42	1.00	0.62	0.60
7	115	8.82	1.19	0.67	0.67
8	123	10.01	1.35	0.70	0.72
9	137	12.08	1.63	0.79	0.80
10	150	13.68	1.85	0.82	0.87
11	161	14.83	2.00	0.85	0.87
12	173	16.03	2.16	0.88	0.89
13	185	17.70	2.39	0.92	0.91
14	196	19.68	2.65	0.97	0.93
15	208	21.68	2.92	1.00	0.93
16	221	23.63	3.19	1.03	0.93
17	233	25.39	3.42	1.03	0.92
18	245	27.09	3.65	1.06	0.91
19	257	28.69	3.87	1.06	0.89
20	271	30.75	4.15	1.06	0.88
21	282	32.15	4.33	1.03	0.87
22	294	33.61	4.54	1.04	0.86
23	312	35.91	4.85	0.91	0.87
24	319	36.80	4.96	0.98	0.88
25	330	37.77	5.10	0.95	0.90
26	339	38.57	5.20	0.95	0.90

TABLE VIII

Absorption of Additive by Baragel Grease, BOA, Permeating Oil Contained 1.0% PAN Additive.

Sample No.	Hours	Volume cc	Volume Oil Volume Sample	% Additive in Oil	% Additive in Grease
1	13	2.17	0.29	0.22	0.23
2	27	4.82	0.65	0.51	0.43
3	58	8.97	1.21	0.57	0.68
4	72	10.23	1.38	0.59	0.74
5	90	11.63	1.57	0.60	0.82
6	116	13.41	1.81	0.60	0.93
7	133	15.20	2.05	0.65	1.00
8	157	17.46	2.36	0.65	1.12
9	183	19.46	2.62	0.67	1.21
10	205	21.49	2.90	0.69	1.30
11	229	23.69	3.20	0.72	1.39
12	241	24.65	3.33	0.74	1.43
13	253	25.55	3.45	0.74	1.46
14	277	27.10	3.66	0.81	1.50
15	299	29.23	3.95	0.85	1.56
16	328	31.98	4.31	0.88	1.61
17	348	33.93	4.57	0.90	1.64
18	365	36.23	4.90	0.96	1.66
19	390	38.22	5.16	0.98	1.67
20	412	39.63	5.35	1.00	1.67
21	434	40.99	5.53	0.96	1.68
22	461	42.67	5.75	1.06	1.66
23	496	44.51	6.01	0.93	1.67
24	518	45.76	6.17	0.91	1.69
25	541	47.89	6.45	0.93	1.72
26	568	49.39	6.65	0.93	1.76
27	589	50.61	6.83	0.89	1.77
28	603	51.61	6.96	0.98	1.78
29	615	52.46	7.07	1.02	1.79

TABLE IX

Data for Permeability Tests on Lithium-Calcium Grease LA

Time, hrs	Run 1	Run 2	Run 3
	Height, cm		
0	29.00	29.95	29.50
2	28.00	-	-
3	-	28.70	28.25
4	27.25	28.25	-
6	-	27.45	26.75
12	24.25	25.10	-
13	23.95	-	-
14	-	24.35	-
15	24.30	24.05	26.80
16	22.80	-	26.00
22	-	21.70	-
24	20.45	-	20.00
25	-	20.85	-
26	-	20.55	19.30
27	19.60	-	-
29	19.00	-	-
30	18.75	-	18.10
32	-	18.85	17.50
33	-	18.55	-

TABLE X

Data for Permeability Tests on Lithium-Calcium Grease LB

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	29.00	29.70	27.90
2	28.00	29.00	27.00
3	27.75	28.75	-
5	27.25	-	-
6	27.05	-	27.30
7	26.85	27.80	-
8	-	27.60	27.05
9	26.45	27.40	-
11	25.95	-	-
20	-	25.00	25.90
21	23.80	24.75	-
24	23.25	24.15	25.50
26	22.80	-	-
27	-	23.50	-
28	22.45	-	25.20
29	-	23.15	-
30	22.05	23.00	25.00
31	21.85	-	-

TABLE XI

Data for Permeability Tests on Lithium-Calcium Grease LD

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	27.95	28.95	29.50
2	-	28.75	29.40
3	27.80	-	-
4	-	-	29.25
6	-	28.55	29.20
15	27.25	-	-
16	27.20	-	-
17	-	28.00	-
20	27.00	27.85	28.50
23	-	27.70	28.35
24	26.80	27.65	-
27	26.65	-	-
37	-	-	27.60
38	-	27.00	-
39	26.15	-	-
40	26.10	26.90	27.50

TABLE XII

Data for Permeability Tests on Lithium-Calcium Grease LE

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	29.50	28.25	30.50
1	28.20	27.00	-
2	27.15	26.00	28.25
3	-	24.95	27.10
4	25.20	-	-
5	-	23.25	-
6	23.20	-	24.25
7	22.45	-	-
9	20.55	-	21.70
12	-	17.75	-
14	17.15	-	-
16	15.90	-	16.75
19	14.25	-	15.00
20	-	13.20	14.45
21	-	12.70	-
23	12.25	11.75	-
24	11.80	11.30	-

TABLE XIII

Data for Permeability Tests on Lithium-Calcium Grease LF

Time, hrs	Run 1	Run 2	Run 3
	Height, cm		
0	29.30	28.50	30.00
1	29.00	28.25	-
2	-	28.00	29.45
3	28.50	-	-
5	-	27.25	-
7	-	26.75	28.20
15	25.75	-	-
17	-	24.60	-
18	25.20	-	25.70
20	24.75	-	-
23	-	23.45	-
25	23.75	-	24.25
27	23.35	22.70	23.75
34	-	21.40	-
35	-	21.20	22.20
39	21.20	-	-
40	21.00	-	-

TABLE XIV

Data for Permeability Tests on Lithium-Calcium Grease LG

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	28.00	29.50	28.70
1	27.75	-	-
2	-	29.00	28.40
3	27.55	-	28.25
4	-	28.70	-
7	-	28.35	27.75
12	26.45	-	27.15
13	26.35	-	-
16	26.00	-	-
18	25.75	27.00	26.50
20	-	26.75	-
22	25.25	-	-
24	25.05	26.25	25.80
32	-	25.45	24.80
33	24.10	25.30	-
34	24.00	-	24.70

TABLE XV

Data for Permeability Tests on Lithium-Calcium Grease LJ

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	30.00	28.50	29.50
1	29.80	-	-
2	-	28.00	29.10
3	29.60	-	-
4	-	27.75	28.90
7	-	27.30	-
15	28.15	-	27.50
16	28.00	-	-
18	27.75	-	27.15
20	27.55	25.80	-
22	-	25.60	-
23	-	25.50	26.50
24	27.10	-	26.45
25	26.95	25.20	-
27	26.75	-	26.15
34	-	24.30	-
36	-	24.10	25.15
39	25.50	-	24.80
40	25.40	-	-

TABLE XVI

Data for Permeability Tests on Lithium-Calcium Grease LK

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	28.40	27.50	29.50
1	28.00	-	-
2	27.70	26.80	28.60
3	-	26.65	-
4	-	26.30	28.00
9	-	25.00	-
11	-	24.50	-
13	24.75	-	-
14	24.55	23.75	-
15	24.30	-	25.00
18	23.45	-	-
20	23.05	-	23.25
24	22.00	-	-
27	-	20.80	22.10
29	-	20.40	21.60
31	-	20.00	21.20
32	-	19.75	-
36	19.60	-	-
37	19.30	-	-

TABLE XVII

Data for Permeability Tests on Baragel Grease BA

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	27.95	27.20	28.90
2	27.45	-	28.40
3	-	26.70	-
4	27.00	26.50	27.80
5	-	26.20	-
7	26.25	25.70	-
13	25.10	-	25.70
15	24.60	-	25.20
16	-	-	-
17	24.25	23.55	24.75
19	-	23.15	24.30
20	23.75	-	-
21	-	22.85	23.95
22	23.25	-	-
24	22.85	-	-
25	22.70	22.00	-
29	-	21.25	22.30
31	21.60	20.80	21.90

TABLE XVIII

Data for Permeability Tests on Baragel Grease BB

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	26.80	26.50	29.00
2	26.55	-	28.80
5	-	25.90	-
7	25.80	25.50	-
8	25.75	25.45	27.80
13	25.05	-	27.05
14	25.00	-	-
17	-	24.30	-
19	24.35	24.10	26.50
20	24.20	24.00	26.10
22	-	23.75	-
23	23.85	-	25.70
24	23.70	-	-
27	-	23.15	-
30	23.00	22.80	24.75
32	22.70	-	24.50

TABLE XIX

Data for Permeability Tests on Baragel Grease BC

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	26.90	28.40	28.80
2	26.75	-	28.70
3	-	28.00	28.50
4	26.65	28.15	-
5	-	28.05	28.35
6	26.45	27.95	-
7	-	27.85	28.20
16	25.75	27.10	27.15
17	-	27.06	27.05
18	25.55	27.00	27.00
19	-	26.95	26.90
20	25.45	-	26.85
26	25.00	-	26.40

TABLE XX

Data for Permeability Tests on Baragel Grease BD

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	29.10	29.60	28.00
1	28.75	-	-
2	28.70	29.00	27.75
3	28.35	28.90	27.70
5	-	28.75	27.55
9	-	28.50	-
13	27.90	-	-
19	27.60	-	26.85
20	-	27.90	26.80
21	27.50	27.85	-
23	27.40	-	-
24	-	27.75	-
25	27.30	-	27.30
27	27.25	27.50	27.25

TABLE XXI

Data for Permeability Tests on Baragel Grease BE

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	24.90	25.00	27.40
2	23.00	-	25.70
3	-	22.25	-
4	-	21.20	23.30
6	19.50	19.50	21.50
7	-	18.85	-
8	-	18.10	-
13	14.50	-	15.90
16	12.75	-	14.00
18	11.75	11.80	12.80
19	11.30	11.30	-

TABLE XXII

Data for Permeability Tests on Baragel Grease BF

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	27.50	27.30	29.00
2	26.95	-	28.20
3	26.55	26.45	-
4	-	26.10	-
5	25.95	25.80	27.30
6	25.65	25.45	-
7	25.35	25.15	26.55
16	22.90	22.75	24.05
17	-	22.45	-
18	-	22.25	23.55
19	22.20	22.05	23.30
21	21.75	-	-
23	21.25	21.60	22.30
27	-	20.00	21.25
29	24.85	-	-
30	24.70	-	20.60

TABLE XXIII

Data for Permeability Tests on Baragel Grease BG

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	28.30	27.50	29.20
2	27.70	26.80	-
4	27.30	-	28.50
5	-	26.30	-
6	26.90	-	28.20
10	-	25.60	27.60
12	-	25.30	-
17	25.50	-	26.60
20	25.00	-	26.20
22	24.75	24.00	-
25	24.30	23.70	-
27	24.20	23.25	25.30
30	-	23.00	24.85

TABLE XXIV

Data for Permeability Tests on Baragel Grease BH

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	27.50	29.20	28.55
3	-	29.00	28.35
4	-	28.90	-
5	25.20	-	28.25
6	27.05	28.75	-
7	26.90	-	28.21
8	26.85	28.60	-
9	-	-	27.95
12	-	28.40	27.75
16	26.40	-	-
19	26.15	-	27.30
20	26.10	27.85	-
23	-	27.70	27.00
26	-	27.50	26.75
28	25.55	-	-
30	25.40	-	26.50

TABLE XXV

Data for Permeability Tests on Baragel Grease BJ

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	26.60	29.00	28.05
1	-	28.60	-
3	26.10	-	28.60
4	-	28.05	-
6	-	27.75	-
7	25.60	-	27.00
8	-	27.50	-
9	25.30	-	26.70
10	25.20	-	-
12	24.90	-	26.25
19	-	25.95	25.25
21	23.80	25.70	-
22	-	25.55	24.85
24	23.40	-	-
29	-	24.70	28.95
32	-	24.25	23.55
33	-	24.15	23.40
35	22.20	-	-
36	22.05	-	-

TABLE XXVI

Data for Permeability Tests on Baragel Grease BK

	Run 1	Run 2	Run 3
Time, hrs	Height, cm		
0	26.65	28.35	29.30
2	26.05	27.60	28.60
4	-	27.00	28.00
5	25.15	-	-
6	24.90	26.40	-
7	24.55	-	27.05
9	-	25.55	-
11	-	25.00	25.90
12	23.25	-	-
16	22.25	-	24.55
19	21.50	22.75	-
20	21.25	-	23.50
23	-	22.00	-
25	-	-	-
26	-	21.25	22.05
28	19.40	-	21.55
30	19.00	20.40	21.05

TABLE XXVII

Data for Permeability Test with Filters And Screens Only

Time, Min.	Height, cm
0	29.10
1.5	28.35
3	27.20
4	26.45
10	23.20
13	21.45
16	20.05
27	15.50
31	14.00
42	10.90
45	10.20

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IX. VITA

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